A

compilation of the research papers submitted to the

ALIGARH MUSLIM UNIVERSITY

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for the fulfilment of the requirement of the award of the

degree of

DOCTOR of SCIENCE

NASEER AHMAD

M.Sc., Ph.D. (ALIG.)

Visiting assistant Professor
Chemistry Department
Louisiana State University

READER
Chemistry Department
Aligarh Muslim University

Dedicated

to

the

memory

of

my

father,

the

warmth

of

whose

affection

I

have

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far

ever

Preface and Acknowledgement

This is a compilation of my 74 research papers (65 published, 2 in press and 7 accepted for publication). The other twelve research papers, under communication, have not been included.

These research papers fall broadly in the domain of coordination chemistry and organo-metallic chemistry, which is expanding with a swift pace. This field is developing in theory and is employing variegated physico-chemical tools and many sophisticated modern experimental techniques. This necessitates collaboration in research and results into publication of research papers in joint authorship. Single authored papers in this field are almost nill in the present day literature.

The present compilation does not include any single authored research papers. Some of the research papers are based on the work done by my students under my supervision and guidance at the Department of Chemistry, Aligarh Muslim University, Aligarh, India and there are others which are based on my own reserch work as a postdoctoral research associate at the Department of Chemistry, Louisiana State university, Baton Rouge, LA 70[illegible] USA with Professor M. C. Day and Professor Joel Selbin; and also as Science Reserach Fellow at King's College, University of London, Strand, London WC[illegible] UK with Professor S. D. Robinson.

I wish to give vent to my feelings of gratefulness to late Dr. M. Farooq, Dr. A. R. Kidwai, Dr. W. Rhman, Heads of Department of Chemistry, Aligarh Muslim University, Aligarh for encouragement and for providing facilities for research during the period 1957 onward. I would like to express my deep sense of gratitude to Professor M. C. Day, for not only showing me the way to excellent research but also for showering his benevolence and erudition on me. Notning can erase the memories of my

association with him. I am also indebted to Professor S. D. Robinson who evinced what a living embodiment of courtesy and politeness can be. I had a 'professionally very successful' year with him. The hardships of London's life were washed away every day by his fascinating and charming behaviour. Frequently I ruminate those remembrances. I owe my thanks to Professor Joel Selbin and professor N. S. Bhacca with whom I had a fruitful scientif association.

I may take this opportunity to express my love and affection to and appreciation of my studens Mr. M. T. Siddiqi, Dr. S. M.S. Akhtar and Dr. S. S. A. Rizvi who worked with me for their masters; Dr. M. M. Khan, Dr. F. R. Rahmani, Dr. S. Ansari, Dr. S. F. H. Rizvi, Dr. M. Sayeed, Dr. Arvind, Dr. A. Shahma, Dr. M. Rahman, Dr. M. Athar, Mr. B. Khan, Mr. K. Iftikhar, Mr. S. Ahmad, Mr. J. Ahmad and Mr. S. M. Ali who did their predoctoral research with me; and Dr. O. Farooq, Late Dr. J. Ahmad, Dr. V. Kumar, Dr. H. Singh, Mr. A. R. Siddiqi who worked under my partial supervision for their Ph.D. degree and many of these again who did their postdoctoral research with me.

Collaboration in research with Dr. W. U. Malik, Dr. S. M. F. Rahman, Dr. A. U. Malik, Dr. R. J. Singh and Dr. S. A. Nabi is highly appreciated.

My heartiest thanks go to my loving wife, Noor Jahan for providing me a very congenial atmosphere at home, conducive to productive work outside.

I cannot for a moment forget my most revered and beloved personality, the prophet of Islam, whose footprints always guide me to the right track and I bow my head to and prostrate before the Almighty for the gift of life and the attendant virtues and blessings.

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1. Naseer Ahmad and S.M.F.Rahman.

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PRELIMINARY STUDIES ON ALIGARH SOIL

The Variations in pH, Conductivity and b.e.c. of the Soil by the Addition of Organic and Inorganic Manures

By

NASEER AHMAD AND S. M. FAZLUR RAHMAN

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PRELIMINARY STUDIES ON ALIGARH SOIL

The Variations in pH, Conductivity and b.e.c. of the Soil by the Addition of Organic and Inorganic Manures

BY NASEER AHMAD AND S. M. FAZLUR RAHMAN

(Department of Chemistry, Aligarh Muslim University)

Received on January 2, 1958

INVESTIGATIONS based on the determination of pH values of soil under changing physical, chemical and biological conditions, present a complex yet interesting aspect of study. In spite of the fact that a number of workers (Daikuhara,[1] Kappen,[2] Paver and Marshall,[3] Page,[4] Magistad,[5] Kelley and Brown,[6] Mattson[7] and Mukherjee *et al.*[8]) have tried to find out the factors responsible for changes in the pH of the soils, the problem is still in a controversial stage and no unanimity of opinion regarding the nature of the reactions responsible for the variations is to be found. The various views are (i) hydrolysis of exchanged aluminium and iron ions, (ii) replacement of H ions by the added salts which in their turn dissolve aluminium or iron oxide present in the soil, and (iii) the influence of CO_2 concentration in soil water system.

Besides determining the changes in pH and conductivity, another interesting method which could be employed for studying and characterizing the soil, is to observe their b.e.c. The method has been successfully used by a number of workers, namely, Hissink,[9] Smith,[10] Kelley and Brown,[11] Page and Williams,[12] Crowther and Basu[13] and Gedroiz.[14]

Mukherjee and co-workers[15] as also Rai Chowdhury[16] have extensively worked on the electrochemical properties and b.e.c. of the Indian soils as well as bentonite clays and have established interesting results correlating the properties of such clays and those of parent minerals. Bhattacharya and co-workers[17] investigated the changes in b.e.c. of different clays under natural conditions of soil formation by mixing the clays with organic matter like leaves and cowdung.

The present communication deals with our results on the variations in the pH and conductivity and exchangeable Ca, Na, K & Mg, in some samples of Aligarh soil by the addition of artificial manures, *viz.*, ammonium sulphate, ammonium nitrate, urea and ammonium hydrogen phosphate and also organic manure obtained by mixing dry and green leaves and cowdung.

EXPERIMENTAL

The following procedure was adopted for the determination of pH, conductivity and b.e.c. of soil samples containing (i) artificial fertilizers and (ii) organic manure consisting of dry and green leaves and cowdung.

TABLE I

Time in days	0	20	30	40	45	60	65	80	84	90
				Determination of pH						
A. With Inorganic manures—										
(1) Amm. sulphate ..	7·62		7·28		7·22		7·19		7·06	7·00
(2) Amm. nitrate ..	7·62		7·34		7·26		7·22		7·22	7·12
(3) Urea	7·62		7·28		7·23		7·10		7·00	6·94
(4) Amm. H. phosphate	7·62		7·28		7·18		7·00		6·96	6·98
B. With Organic manure—										
(1) Sample No. 1 ..	7·20	7·30		7·60		8·20		8·20		8·00
(2) Sample No. 2 ..	7·15	7·10		8·10		8·50		8·42		8·36
(3) Sample No. 3 ..	7·26	7·30		7·44		8·20		8·10		7·95
				Determination of Conductivity						
A. With Inorganic manures—										
(1) Amm. sulphate ..	2·40		36·2		24·8		23·8		22·8	$22·5 \times 10^{-3}$
(2) Amm. nitrate ..	2·40		36·0		26·0		23·5		23·5	$26·0 \times 10^{-3}$
(3) Urea	2·40		29·0		26·0		24·0		23·5	$26·0 \times 10^{-3}$
(4) Amm. H. phosphate	2·40		32·0		29·0		25·5		22·5	$22·0 \times 10^{-3}$
B. With Organic manure—										
(1) Sample No. 1 ..	38·6	34·0		20·0		17·3		28·5		$34·2 \times 10^{-5}$
(2) Sample No. 2 ..	34·0	31·0		23·0		30·2		36·5		$34·5 \times 10^{-5}$
(3) Sample No. 3 ..	56·0	38·0		25·5		32·5		39·5		$38·0 \times 10^{-5}$

Soil samples obtained by passing through 2 mm. sieve were mixed with different fertilizers, *viz.*, ammonium sulphate, ammonium nitrate, urea and ammonium hydrogen phosphate (5 gm. of each fertilizer for 500 gm. of soil). The prepared soil was transferred to four earthenware pots. These were kept buried $\frac{3}{4}$ of their height under the sun for a period of 3 months and were watered twice a day during the course of experiment. For examining conditions after the addition of organic manures, three different samples of soil of the same dispersity as given above were taken and mixed with leaves (dry and green), and cowdung. These were transferred to earthenware pots and subjected to similar conditions of exposure as described above and variations observed for the same period as in the case of artificial manuring. The variations in pH and conductivity at different intervals of time were determined by taking the supernatant liquid obtained by thoroughly shaking 5 gm. of air-dried soil in 50 c.c. of conductivity water. All measurements were made by Lange's Acidometer and W.T.W. Conductivity Bridge.

The soil samples were periodically analysed for exchangeable cations by leaching with ammonium chloride, and the exchangeable calcium was estimated as oxalate, magnesium as pyrophosphate, sodium as uranyl acetate and potassium as cobalto-nitrite.

The results on pH, conductivity and base exchange capacity of different soil samples are given in Tables I and II.

TABLE II

Time in days	0	20	30	40	45	60	65	80	84	90
Determination of Exchangeable Calcium (M.E. %)										
A. With Inorganic manures—										
(1) Amm. sulphate ..	4·16		18·68		18·45		18·32		17·00	16·90
(2) Amm. nitrate ..	4·16		18·96		18·62		16·94		..	18·62
(3) Urea	4·16		18·02		17·86		17·54		..	17·4
(4) Amm. H. phosphate	4·16		18·66		17·96		17·66		.	17·4
B. With Organic manure—										
(1) Sample No. 1 ..	7·7	13·5		23·7		9·0		2·5		1·0
(2) Sample No. 2 ..	7·5	6·05		5·0		4·5		2·5		traces
(3) Sample No. 3 ..	9·5	15·0		6·0		0·15		0·13		0·05
Determination of Exchangeable Sodium (M.E. %)										
A. With Inorganic manures—										
(1) Amm. sulphate ..	0·57		1·88		2·00		2·12		2·22	2·51
(2) Amm. nitrate ..	0·57		2·00		2·01		2·11		2·12	2·35
(3) Urea	0·57		1·86		1·88		1·94		1·98	2·00
(4) Amm. H. phosphate	0·57		2·02		2·16		2·30		2·20	2·00
Determination of Exchangeable Potassium (M.E. %)										
A. With Inorganic manures—										
(1) Amm. sulphate ..	0·44		0·96		0·82		0·80		0·76	0·75
(2) Amm. nitrate ..	0·44		0·966		0·82		0·83		0·81	0·76
(3) Urea	0·44		0·92		0·84		0·86		0·82	0·75
(4) Amm. H phosphate	0·44		0·98		0·86		0·77		0·73	0·72
Determination of Exchangeable Mangesium (M.E. %)										
A. With Inorganic manures—										
(1) Amm. sulphate ..	1·62		5·60		5·66		5·69		5·14	7·20
(2) Amm. nitrate ..	1·62		5·38		5·56		6·08		..	6·50
(3) Urea	1·62		5·36		5·32		5·23		..	5·70
(4) Amm. H. phosphate	1·62		5·56		5·64		5·86		..	5·80

DISCUSSION

The data on the variations in pH values and conductivity by the addition of inorganic and organic substances show the following:—

1. The pH value of the soil sample gradually decreases with time on the addition of artificial manures during a period of 3 months.

The conductivity values under similar conditions however show an initial increase followed by a continuous decrease after a period of about 1 month.

2. On the other hand, the pH values with organic manures show a behaviour different from those for inorganic ones. The pH values show an increase for a considerable time (a slight decrease only after about 2½ months) for all the three soil samples. The variations in conductivity show a periodicity under similar conditions.

The interesting observations in tables and curves are that the pH values are higher by the decomposition of organic substances in the soil than those obtained by the hydrolysable inorganic salts. The conductivity values, however, show a less regular trend, although according to the high mobility of H-ions, the conductivity should be higher when pH values are low and *vice versa*. But the results show that the changes in pH and conductivity appear to be connected by more than one factor than the H-ion alone. The hydrolysable inorganic salts should give more H-ions by hydrolysis than the organic acids formed during the decomposition of organic matter, but it is not yet known to what extent the mechanism of the changes in pH and conductivity is governed by H-ion concentration, mineralisation of the organic matter (cowdung and leaves, etc.) and the role of microbial population in the system. Conductivity may increase in spite of the less proportion of H-ions (*i.e.*, higher pH values), provided mineralisation is great and this probably is true in many cases. The micro-organisms can also be effective in reducing the conductivity during their growth by the assimilation of inorganic salts which results in minimising the concentration of the water-soluble salts. Our data are in support of the above observations which seem to be responsible for the changes in conductivity.

Adsorption of cations and ions by the soil colloids is also an important factor to influence the pH and conductivity in the system during the decomposition of the inorganic and organic matter in the soil. Moreover, the buffering capacity of the amphoteric clay complex plays no less an important part in the variations of pH and conductivity.

Daji[18] observed that the soil tends to become alkaline in later stages by the effect of green manuring but Stephenson[19] observed that the soil becomes alkaline during the earlier stages but acidic later on. Bhattacharya and Bansal[20] observed that when there was a fall in pH, the conductivity generally rises and concluded that the frequency of the rise and fall of pH and conductivity was specific with the nature and the composition of the raw organic matter and also with the character of the soil. Our experiments were continued for 3 months only, yet the general trend of our observations is in agreement with the conclusion made by the previous workers.

Experimental results on the exchangeable cations in the case of various soil samples by the addition of artificial manures show that there is not any remark-

able difference of the added manures on the b.e.c. of the soil. It will, however, be of interest to note that during the first 30 days Ca and K show a very large increase in their exchangeability followed by a more or less regular decrease. The variations of exchangeable Na and Mg with time however are less striking than either Ca or K. Since exchangeable Ca plays an important role in the fertility of the soil, the b.e.c. for this cation was also studied with soils to which organic manure was added. It will be observed from the tables that the exchangeable Ca increases for the first 40 days in Soil No. 1 and for 20 days in Soil No. 3 while there is a continuous decrease of exchangeable Ca in Soil No. 2. It seems that this property is specific for the particular soil used. It may further be added that the addition of artificial manures brings about a sudden increase in the b.e.c. of the soil when compared to the action of organic manure.

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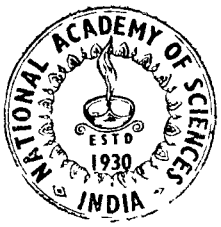
PRELIMINARY STUDIES ON ALIGARH SOIL

Chemical Analysis of Differnt Soil Samples from the University Campus

By

NASEER AHMAD AND S. M. FAZLUR RAHMAN



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PRELIMINARY STUDIES ON ALIGARH SOIL

Chemical Analysis of Different Soil Samples from the University Campus

BY NASEER AHMAD AND S. M. FAZLUR RAHMAN

(Department of Chemistry, Aligarh Muslim University)

Received on April 19, 1958

THE various physico-chemical properties of Aligarh soil seem to be very much influenced by the defective drainage of the water used for its irrigation. It appears that due to this defect the salts from the waters are continuously being added to soil resulting in an increase in the salinity. Considering this factor in view it was thought worthwhile to carry out an analysis of various soil samples from different areas in the University campus. The results on the amount of various cations like Ca, Al, Fe, Mg, K, Na and ammonium and anions, *viz.*, silicate, CO_3, phosphate and nitrates and on the total water-soluble salts, water-holding capacity, carbon, nitrogen, loss on ignition and pH are communicated in this paper.

EXPERIMENTAL

Soil samples were collected from different places around the University, by digging a hole (diameter 6″) upto 6″, in the ground and obtaining the soil from five such holes dug in the same field. The soil thus obtained was powdered, mixed thoroughly, passed through a 2 mm. sieve and a part of it was dried in air for about a week. Such soil samples were analysed for different constituents.

(1) *Analysis for cations and anions.*—Ca, Na and K were estimated by the Flame photometer (Lange). A weighed amount of the soil was taken and dissolved in concentrated HCl. The solution was analysed for Ca, Na and K by Flame photometer and iron by colorimeter (Lange) using ammonium sulphocyanide as colouring agent. Aluminium was estimated as Al_2O_3 by precipitating $Al(OH)_3$ and $Fe(OH)_3$ and substracting the amount of Fe_2O_3 from the weight of Al_2O_3 and Fe_2O_3. The MCl insoluble portion was weighed and reported as SiO_2. Mg was estimated as pyrophosphate and phosphorus by the ammonium molybdate method. Carbonate was determined by passing the CO_2 evolved (on treatment with H_2SO_4) through standard baryta solution. The procedure adopted for the estimation of nitrate was that of leaching a weighed amount of soil (10 gm.) on a Buchner funnel by dilute H_2SO_4 solution. The leachate was boiled with MgO until it was reduced to half its original volume. The solution was cooled and zinc dust (5 gm.), caustic soda solution (30% 70 c.c.) and powdered iron (5 gm.) added in the above order. The solution was then distilled in a nitrogen distillation apparatus for about one hour and the evolved ammonia was collected in a standard HCl solution. The solution was then titrated with NaOH solution of known concentration and as usual the amount of nitrate was calculated. For ammonia the soil was shaken with N NaCl solution and filtered. The soil was washed with N NaCl and the filtrate was boiled with magnesia and the evolved NH_3 was absorbed in standard HCl and then titrated.

The result for SiO_2, CO_3, CaO, Al_2O_3, Fe_2O_3, MgO, K_2O, Na_2O, P_2O_5, NO_3 and NH_3 are given in Table I.

TABLE I

Soil Sample No.	SiO_2	CO_3	CaO	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	P_2O_5	NO_3	NH_3
1 From a lawn, isolated from adjacent areas	86·7	0·51	1·5	1·63	3·58	0·108	0·082	0·083	0·128	0·0049	0·0018
2 S W. of Aligarh, cultivation of gram	88·33	0·77	0·48	2·73	2·7	0·121	0·11	0·351	0·134	0·0061	0·0031
3 N.-W. of Aligarh, Marshy ..	86·79	0·72	2·72	2·199	3·0	0·213	0·16	0·24	0·0671	0·0018	0·0012
4 W. of Aligarh ..	83·276	0·802	0·522	2·70	4·6	0·135	9·408	0·428	0·0335	0·0025	0·0014
5 Near a distributary of Canal ..	90·396	0·832	0·495	1·037	2·73	0·992	0·15	0·395	0·096	0·001	..
6 Soil compact, very hard ..	78·84	0·61	0·197	2·64	4·68	0·091	0·249	1·90	0·0832	0·0015	0·0011
7 Clay in abundance, dry .	83·31	0·306	1·32	0·73	4·26	0·216	0·225	1·16	0·069	0·0022	..
8 From Garden of Fort ..	88·77	0·41	0·52	2·39	5·64	0·134	0·285	0·32	0·0238	0·0089	0·0062
9 From Bhamola ..	90·55	0·512	0·40	1·37	2·2	0·210	0·14	0·284	0·0215	0·0056	0·0021
10 From behind V M Hall ..	78·83	0·77	0·88	6·15	10·92	0·248	0·218	0·448	0·071	0·001	..
11 Chaoultala Village ..	89·691	0·821	0·02	0·27	4·32	0·101	0·15	0·348	0·065	0·0025	..
12 West to the Fort, slopy ..	85·25	0·853	1·3	..	6·5	0·66	0·856	0·83	0·182	0·0038	0·0026
13 From a lawn ..	84·25	0·234	0·2	2·97	5·64	0·123	0·46	0·40	0·153	0·0058	0·0031
14 From Agriculture Farm ..	86·6	1·58	1·21	3·213	2·57	0·336	0·178	0·788	0·985	0·0046	0·0068
15 Behind Minto Circle ..	76·6	1·57	0·65	6·64	2·36	0·083	0·82	4·10	0·098	0·0028	0·0013
16 V. M. Hall Lawn .	79·62	0·972	0·80	5·029	2·16	0·83	0·63	2·52	0·048	0·0039	0·0036
17 From a cane sugar field, fertilizer used	72·89	1·957	0·889	5·21	3·12	1·82	0·738	0·283	0 2325	0·0031	0·0013

(2) Total nitrogen was estimated by Kjeldahl's method using salicylic acid reduction method. The total carbon was estimated by the method of Robinson, Mc Leau and Williams (4th Edn. Knowles & Watkins, p. 46). For water-soluble salts, weighed amount of soil was shaken with distilled water and filtered. The filtrate was evaporated to dryness and the solid weighed as total water-soluble salts. For loss on ignition a blank experiment was performed by igniting a weighed amount of the soil.

(3) *The water-holding capacity.*—This was estimated by taking 200 gm. of soil sample on a filter-paper wetting it with water and then taking the weight after 5 hours. For pH measurements Lange's Acidometer was used. The results for total carbon, nitrogen, water-soluble salts, loss on ignition, water-holding capacity and pH are given in Table II.

TABLE II

Sample No.	Total Carbon	Total Nitrogen	Water-soluble salts	Loss on ignition	Water holding capacity	pH
1	0·45	0·0808	0·78	4·71	23·0	6·8
2	0·293	0·0721	0·95	3·57	17·2	7·0
3	0·186	0·0321	0·931	2·6	17·3	6·9
4	0·603	0·076	0·13	5·85	33·2	7·8
5	0·404	0·012	2·73	3·47	22·2	9·3
6	0·586	0·051	0·98	6·54	26·6	7·2
7	0·422	0·063	0·85	3·52	29·0	7·8
8	0·08	0·093	0·35	1·44	39·4	7·6
9	0·095	0·0825	0·39	1·68	45·8	7·3
10	0·34	0·0123	0·687	0·944	64·0	7·4
11	0·15	0·0232	0·0021	1·112	49·6	7·1
12	0·34	0·0543	0·42	2·276	49·2	7·05
13	0·468	0·0768	0·251	4·41	22·3	7·02
14	0·312	0·093	0·231	4·52	28·3	7·22
15	0·326	0·0362	0·624	4·72	53·3	8·47
16	0·263	0·046	0·315	4·86	26·6	7·62
17	0·3121	0·0833	0·187	6·30	23·6	7·3

DISCUSSION

The analysis of various samples tabulated above shows that our soil is deficient in nitrogen, phosphorus and carbon. This may be due to the salinity

of the soil which does not allow perennial grasses to grow in abundance. Hence organic matter and nitrogen which are added by the decay of grasses are not provided to the soil in adequate quantities. The increased amount of water-soluble salts confirms the postulate that the salts of irrigation water are being accumulated in our soil and are not being leached away as the natural drainage is defective and no appropriate steps have been taken to make it efficient artificially.

[Jour. Indian Chem. Soc., Vol. 40, No. 7, 1963]

Studies on Some Less Familiar Ferrocyanogen Complexes. Part XIV. Composition, Properties, and Colloidal Behaviour of Titanium (III & IV) Ferricyanides

Naseer Ahmad, S. M. Fazlur Rahman, and Wahid U. Malik

Ti(III & IV) ferrocyanogen complexes have been prepared by mixing the reactants in equimolecular proportions. The dried precipitates have the compositions $KTi^{III}Fe^{II}(CN)_6$, $Ti^{IV}Fe^{II}(CN)_6$, and $Ti^{III}Fe^{III}(CN)_6$. The freshly precipitated complexes exhibit both hydrolytic and adsorptive properties. $KTi^{III}Fe^{II}(CN)_6$ and $Ti^{IV}Fe^{II}(CN)_6$ hydrolyse more than $Ti^{III}Fe^{III}(CN)_6$ does. Unlike other metal ferro- and ferricyanides, the metal ion is adsorbed more than the ferrocyanogen ions. Titanic ferrocyanide could be obtained as a negatively charged sol by mixing $TiCl_4$ and $K_4Fe(CN)_6$ in the ratio of 0.89:1 respectively.

The results of conductometric, thermometric, and potentiometric titrations, carried out both in the direct and reverse order, confirm the results of chemical analysis and also provide evidence for the adsorption complexes.

Amongst the metallic ferro- and ferricyanides, the study of titanium complexes has received very little attention. Recently amperometric studies on the interaction of Ti(III) with potassium ferro- and ferricyanides and that of Ti(IV) with potassium ferrocyanide were carried out in this laboratory[1]. The results obtained, although not conclusive, were interesting enough and hence needed a more systematic and critical study. This communication deals with our investigations on the properties, colloidal behaviour, and composition of these complexes.

EXPERIMENTAL

To a solution of titanous chloride (150 ml, 12.5% w/v, containing 12.5% HCl) was added specially pure titanium metal (10 g.) and dry HCl gas was passed into it. $TiCl_3.6H_2O$ crystals[2] were dissolved in air-free, double distilled water; the strength was determined by adding a known volume to an acidified ferric alum solution and titrating the resulting ferrous sulphate against potassium permanganate. A layer of kerosene was kept over the solution throughout the investigation.

Titanium chloride ($TiCl_4$, 12% w/v soln. containing 15% HCl, BDH) was used for preparing the solution and the strength determined as above, after reducing a known volume in Jone's reductor.

Potassium ferro- and ferricyanide solutions were prepared by dissolving A. R. and recrystallised samples respectively in double distilled water. The solutions were stored in amber-coloured bottles and strengths determined by the usual methods[3].

1. Malik, this *Journal*, 1961, **38**, 303.
2. Mellor, "Inorganic and Theoretical Chemistry", Vol. VII, p. 74.
3. Cumming and Kay, "Quantitative Chemical Analysis", 1956. pp. 155, 173.

Analysis of the Complexes.—A 'neutral' sample of titanium(III) ferrocyanide was prepared by adding equal volumes of the reactants of the same concentration (M 10). The precipitate was centrifuged, washed first with water and then with 50% ethanol, followed by final washings with absolute ethanol and ether. The originally yellow precipitate changed to a chocolate-brown colour by this treatment. It was dried for a number of days in a vacuum desiccator over H_2SO_4 (conc.). The 'neutral' complexes of Ti(III) ferricyanide and Ti(IV) ferrocyanide were also obtained in a similar manner. The Ti(III) complex was brownish yellow and the Ti(IV) complex was dark brown in colour.

The method of decomposition of the complex and subsequent estimation of titanium and iron as oxides were the same as used in the analysis of ferrocarbon titanium[4]. Potassium was estimated as dipotassium monosodium cobaltinitrite[5] and the amount of the cyanogen present in the complex was determined by Volhard's method[6]. Experiments were performed in duplicate. The components were found to have the following formulas:

Titanous ferrocyanide: $K_{1\cdot0109}\ Ti_{1\ 0001}\ Fe,\ (CN)_{5\cdot946}$; $K_{1\ 0009}\cdot\ Ti,\ Fe_{1\cdot004}\ (CN)_{5\ 878}$.
Titanous ferricyanide: $Ti_{1\cdot006},\ Fe.\ (CN)_{6\ 004}$; $Ti,\ Fe_{1\cdot018},\ (CN)_{6\ 061}$.
Titanic ferrocyanide: $Ti,\ Fe_{1\cdot\ 67},\ (CN)_{6\cdot493}$; $Ti,\ Fe_{1\cdot048},\ (CN)_{6\ 383}$.

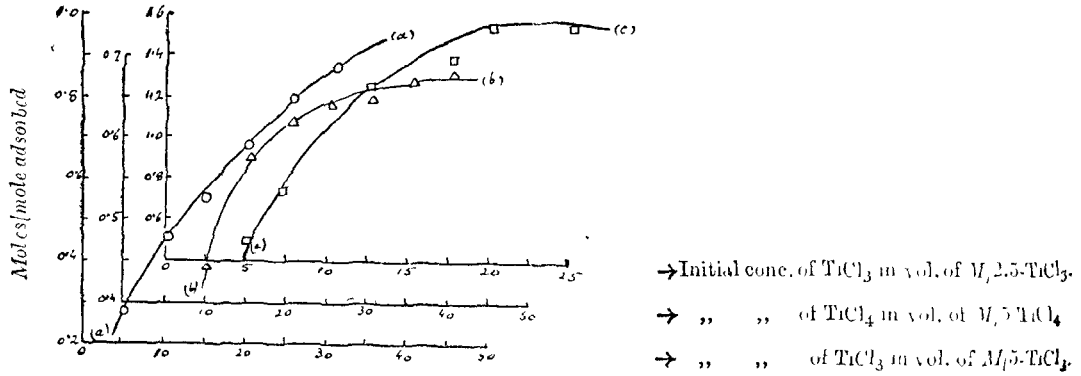

FIG. 1

(*a*) Adsorption of $TiCl_3$ on $K\ Ti^{III}Fe^{II}\ (CN)_6$.
(*b*) ,, ,, $TiCl_4$,, $Ti^{IV}Fe^{II}\ (CN)_6$.
(*c*) ,, ,, $TiCl_3$,, $Ti^{III}Fe^{III}\ (CN)_6$

Titanic Ferrocyanide Sol.—The freshly precipitated complex showed a tendency to pass into the colloidal state on washing either with water or dilute solution of the complexing agent. Determination of optimum conditions for sol formation and study of the colloidal properties were therefore undertaken. On employing the method of double decomposition, it was found that fairly stable sol could be obtained by using a slight excess of *potassium ferrocyanide* [$Fe(CN)_6$: Ti=*1:0.89*]. The usual method of obtaining ferrocyanide sol was employed with the only precaution that fairly dilute solution of titanic chloride was used and it was added dropwise to potassium ferrocyanide solution with constant stirring (mixing the reactants in the reverse order invariably resulted in the formation of a precipitate). The undialysed sol, although negatively charged (as found by electrophoresis in Burton's tube), behaved curiously towards electrolytes. Coagulation experiments with

4. Scott, "Standard Methods of Chemical Analysis", Vol. I, 5th ed., 1939, p. 983.
5. Cumming and Kay, *op. cit.*, p. 382.
6. Scott, *op. cit.*, p. 661.

trolyte, forming what are known as cationic and anionic series, revealed that both ons and anions affected the precipitation to the same extent.

Adsorption.—Adsorption of either of the reactants on the different complexes studied by employing 1 g. of the freshly precipitated compounds. The results are shown by 4. The adsorption of $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$ on their complexes was negative.

Hydrolytic Behaviour.—For studying the hydrolysis of the various complexes, the tions of the reactants for a particular complex were mixed in such quantities as to ride 1.0, 0.75, 0.5, 0.25, and 0.125 g. of the complex in a fixed volume of the suspension ml). Carbon dioxide was then passed through these solutions for 12 hours. The solu- s were centrifuged, the supernatant liquids titrated for ferrocyanide and ferricyanide, ading on the complex used, and the percentage hydrolysis was calculated (Table I).

TABLE I

$Ti^{IV}Fe^{II}(CN)_6$.	% Hydrolysis.	$Ti^{IV}Fe^{II}(CN)_6$.	% Hydrolysis.
1.00g.	35.8	1.00g.	26.3
0.75	35.2	0.75	30.2
0.00	43.3	0.05	31.3
		0.25	55.1
		0.125	86.0

Experiments with titanous ferricyanide showed negligible hydrolysis of the complex.

Conductometric Titrations.—The results of conductometric titration are shown in Fig. 2.

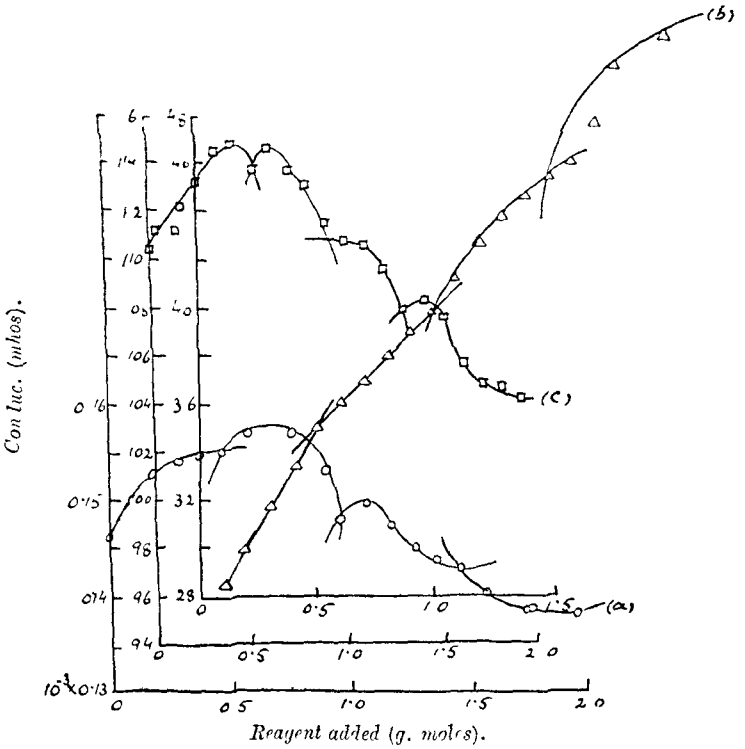

FIG. 2

(*a*) 20 ml of $M/20$-$TiCl_3$ in the cell; $M/10$ $K_4Fe(CN)_6$ added.
(*b*) ,, ,, $M/100$,, ,, ,, : $M/50$ $K_3Fe(CN)_6$,,
(*c*) 40 ,, ,, $TiCl_4$,, ,, ; $M/5$-$K_4Fe(CN)_6$,,

Potentiometric Titrations.—The potentiometric titrations were performed with the help of a Tinsley potentiometer, using a lamp scale outfit. The ferroferricyanide couple was created at the platinum indicator electrode by adding a little potassium ferricyanide to potassium ferrocyanide solution. Titrations with potassium ferricyanide could be carried out even without adding potassium ferrocyanide to the potassium ferricyanide solution (Fig. 3).

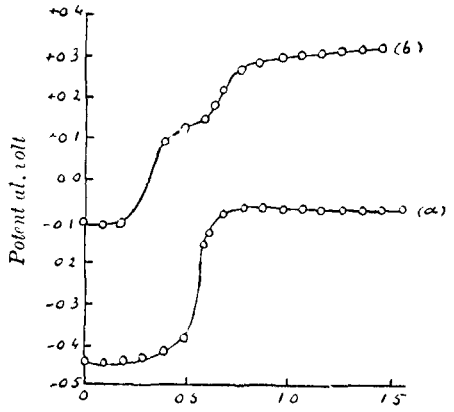

FIG. 3

(*a*) 20 ml of *M*/100,25% alc. $TiCl_3$ in the cell; *M*/50 $K_4Fe(CN)_6$ added.
(*b*) Do; *M*/50 $K_3Fe(CN)_6$ added.

Thermometric Titrations.—For the thermometric titrations, a well-insulated Dewar's flask of 100 ml capacity was used. The burette was wrapped with asbestos on all sides except for the streak left to make the graduations visible. The reactants were kept for sometime to attain room temperature before actually starting the titrations. Variations in temperature were noted by a Beckmann thermometer. Both direct and reverse titrations were carried out (Fig. 4).

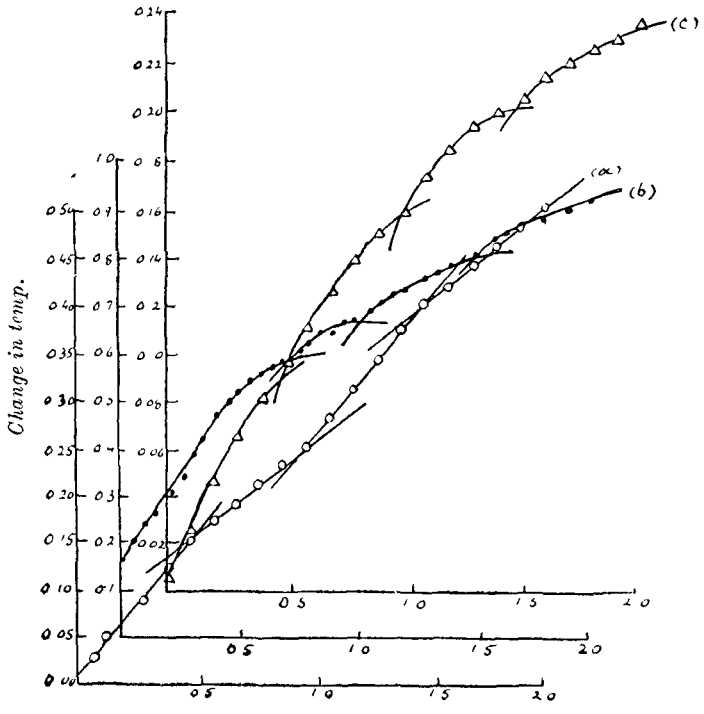

FIG. 4

(*a*) 40 ml of *M*/100 $TiCl_3$ in the cell, *M*/5 $K_4Fe(CN)_6$ added.
(*b*) 30 ,, ,, *M*/60 ,, ,, ,, *M*/20 $K_3Fe(CN)_6$,,
(*c*) 20 ,, ,, *M*/50- $TiCl_4$,, ,, *M*/25 $K_4Fe(CN)_6$,,

DISCUSSION

The fact that titanic ferrocyanide can be dispersed in a fairly stable state by excess of potassium ferrocyanide and that the other complexes also show a tendency to pass into the colloidal state merely by washing, leads to the conclusion that the various complexes could be endowed with high adsorptive capacities. Adsorption experiments, however, do not provide precise information regarding this behaviour since in only two cases, viz., $KTi^{III}Fe^{II}(CN)_6$ and $Ti^{IV}Fe^{II}(CN)_6$, adsorption of the respective metal ion is seen. In other cases an anomalous behaviour creeps in and instead of positive adsorption of either of the reactants, negative adsorption takes place. The anomaly may be explained either by assuming the hydrolysis of the complex or due to swelling of the freshly precipitated complex. Since the latter effect is not marked, the only factor, which can be taken to be operative, is their hydrolysis. Our experiments on the hydrolysis of titanous and titanic ferrocyanides, where this tendency is exhibited to a fairly high degree, lends support to the former postulate.

The results of chemical analysis show that titanous ferricyanide and titanic ferrocyanide may be represented by the formula $Ti^{III}Fe^{III}(CN)_6$ and $Ti^{IV}Fe^{II}(CN)_6$ respectively. It is, however, difficult to say that titanous ferricyanide having the composition $Ti^{III}Fe^{III}(CN)_6$ is really formed in view of a fairly large redox potential existing in the system:

$$Ti^{3+} + Fe(CN)_6^{3-} \rightarrow Ti^{4+} + Fe(CN)_6^{4-}.$$

The value of K for the above reaction (calculated from the oxidation potentials of titanous-titanic and ferro-ferricyanide couples) is 2.7×10^6. Such a large value definitely points towards the oxidation of titanous to titanic and the consequent reduction of the ferricyanide to the ferrocyanide. The reaction of titanous chloride with potassium ferricyanide can thus be represented as:

$$Ti^{3+} + Fe(CN)_6^{3-} \longrightarrow Ti^{4+} + Fe(CN)_6^{4-}$$

$$Ti_4^{+} + Fe(CN)_6^{4-} \longrightarrow TiFe(CN)_6$$

the overall reaction being

$$TiCl_3 + K_3Fe(CN)_6 = Ti^{IV}Fe^{II}(CN)_6 + 3\,KCl.$$

The titanous ferrocyanide is formed by the reaction:

$$TiCl_3 + K_4Fe(CN_6) = K\,Ti^{III}Fe^{II}(CN)_6 + 3\,KCl.$$

Results of conductometric, thermometric, and potentiometric titrations between ...anium salts and the corresponding potassium ferro- and ferricyanide provide enough evidence regarding formation of the complexes of types $KTi^{III}Fe^{II}(CN)_6$, $Ti^{III}Fe^{III}(CN)_6$ and $Ti^{IV}Fe^{II}(CN)_6$, thereby confirming the results on the chemical analysis of titanous ferro- and ferricyanides and titanic ferrocyanide.

A survey of the titration curves would reveal that besides the combining ratio of 1:1 (for which the above mentioned compounds have been enumerated) other combining ratios are possible. Thus the ratios 2:1 and 2:3 [$TiCl_3$: K. $Fe(CN)_6$; vide curve 2a 3a, and 4a] are seen to exist in the case of conductometric (both direct and reverse). thermometric, and

potentiometric titrations. With these ratios the following stoichiometric reactions may be visualised to take place.

$$2TiCl_3 + K_4Fe(CN)_6 \longrightarrow KTi^{III}\,Fe^{II}(CN)_6\,TiCl_3 + 3KCl$$

$$2TiCl_3 + 3K_4Fe(CN)_6 \longrightarrow 2KTi^{III}\,Fe^{II}(CN)_6\,K_4Fe(CN)_6 + 6KCl$$

The formation of the above mentioned complexes appears to be highly probable in view of the fact that the titanous ferrocyanide complexes in their freshly precipitated state are liable to adsorb both titanium and ferrocyanide ions. Useful information on the products of interaction of $TiCl_4$ and $K_4Fe(CN)_6$ is available on the basis of conductometric and thermometric titrations. Here the combining ratios of 2:1 and 2:3 [$TiCl_4$: $K_4Fe(CN)_6$, vide curves 2*c* and 3*c*] are found and therefore complexes of the type of $Ti^{IV}\,Fe^{II}(CN)_6\,TiCl_4$ and $2Ti^{IV}\,Fe^{II}(CN)_6\,K_4Fe(CN)_6$ should be formed. These results not only go to show that both Ti (IV) and $K_4Fe(CN)_6$ are adsorbed by the freshly precipitated complex but it is also found that the metal ion is more strongly adsorbed than the ferrocyanogen ion (0·68 moles of Ti^{IV} per mole of complex). This behaviour, although confirms the results on the adsorptive capacity of titanic ferrocyanide, are in variance with those of other workers for the metal complexes of alkali ferrocyanides.

In the complex formation between $TiCl_3$ and $K_3Fe(CN)_6$, combining ratios [Ti^{3+}: $Fe(CN)_6^{3-}$] such as 3:2, 3:1, and 2:3 (vide curves *b*, Figs. 2—4) are found by the different methods employed. First two ratios again provide strong evidence for the adsorption of metal ion by the freshly precipitated complex and also for the existence of the compounds having the composition $Ti^{III}\,Fe^{III}(CN)_6\,TiCl_3$ and $Ti^{III}Fe^{III}(CN)_6\,2TiCl_3$. The last ratio, viz. 2:3, points towards the formation of the complex $2Ti^{III}\,Fe^{III}(CN)_6 \cdot K_3Fe(CN)_6$ which again appears to be an adsorption complex of titanous ferricyanide.

CHEMICAL LABORATORIES,
MUSLIM UNIVERSITY, ALIGARH

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Studies on the Complexes of Hydrazine with Cobalt Chloride and Sulphate, Zinc Chloride and Sulphate, Nickel Sulphate, Zirconium Sulphate and Copper Chloride

By NASEER AHMAD and S. M. FAZLUR RAHMAN

With 4 figures

Summary

The interaction of hydrazine hydrate with cobalt chloride and sulphate, zinc chloride and sulphate, nickel sulphate, zirconium sulphate and copper chloride was studied employing conductometric and thermometric titrations when the ratios of 1:2, 1·3, 1:2, 1:2, 1:3, 1 1 and 1.2 between hydrazine and the metal salt, respectively, emerged. The precipitates were analysed.

Inhaltsübersicht

Es wurde die Niederschlagsbildung bei der Reaktion verschiedener Schwermetallsalze (Sulfate und/oder Chloride des Co, Zn, Ni, Zr und Cu) mit Hydrazinhydrat konduktometrisch, thermometrisch und analytisch untersucht.

A large number of metal complexes of hydrazine have been prepared

FRANZEN[1]) et al. have reported the preparation of some forty compounds of hydrazine both di and trihydrazinates of mostly metals of the first transition series. They have also reported to have obtained trihydrazinates of Cobalt(II) by warming nitrates or sulphates of cobalt with 50% hydrazine hydrate. SCHRADER[2]) and others have described the preparation of a reddish violet $NiSO_4$, $3N_2H_4$ by treatment of Nickel sulphate with hydrazine hydrate. GILBERT and EVANS[3]) have prepared the nickel hydrazine complexes of sulphate, acetate, benzoate, chloride, bromide, pyrophosphate, oxalate and cyanide. They have suggested that there might be stepwise addition of N_2H_4 to the Ni ion. SCHWARZENBACH and

[1]) H. FRANZEN and O. VON MAYER, Z. anorg. Chem. **60**, 247 (1908); Ber. dtsch. chem. Ges. **39**, 3377 (1906).

[2]) T. CURTIUS and F. SCHRADER, J. prakt. Chem. **50**, 311 (1894).

[3]) E. C. GILBERT and WM. H. EVANS, J. Amer. chem. Soc. **73**, 3516 (1951).

ZOBRIST[4]) have given the solubility products of $Ni(N_2H_4)_3SO_4$ etc. BAILAR[5]) and coworkers have done the polarographic study of the complexes formed between hydrazine and zinc perchlorate. GOGRISHVILI[6]) and others studied the action of hydrazine hydrate and carbon dioxide on Cobalt(III) ammines, $Co(N_2H_4)_2Cl_2$ and trans-$Co(NH_3)_4(NO_2)_2NO_3$. THEY[7]) have also prepared a light blue salt $Ni(N_2H_4)_2Cl_2$ and $Ni(N_2H_4)_2SO_4 \cdot 2H_2O$ from $(N_2H_3COO)_2 \cdot NiN_2H_4$. HOFMANN and MARBURG[8]) described the preparation of $CuCl_2 \cdot 2N_2H_4$ from copper chloride and hydrazine hydrate in alcohol in the form of blue needles.

No reference about the hydrazinates of Zirconium is found in literature. No attempt seems to have been made to ascertain the composition of the insoluble complexes of hydrazine with cobalt chloride and sulphate, zinc chloride and sulphate, Nickel sulphate, and copper chloride by physical methode. We have performed both direct and reverse conductometric and thermometric titrations to study these complexes and have also done the chemical analysis of these complexes to confirm earlier work done.

Experimental

Preparation and standardization of Solutions

10 ml. of 100% hydrazine hydrate (B. D. H.) was diluted to 250 ml. This solution was standardized and used for the preparation of aqueous and alcoholic solutions of hydrazine of various strengths. 10 ml. of this solution was diluted to 100 ml. in a standard flask and strength determined by standard[9]) Ferricyanide method of RAY and SARKAR[10]).

Recrystallised samples of cobalt chloride and cobalt sulphate were used for preparing their solutions and cobalt extimated[11]) by precipitating it with Nitroso-β-naphthol, converting it into $CoSO_4$ and weighing.

Pure iron free zinc sulphate and zinc chloride were used for preparing their solutions and zinc estimated[12]) volumetrically by titrating against standard[13]) ferrocyanide.

Nickel sulphate solution was prepared by dissolving recrystallised Nickel sulphate in conductivity water and nickel extimated[14]) as nickel dimethyl glyoxime.

[4]) G. SCHWARZENBACH and A. ZOBRIST, Helv. chim. Acta **35**, 1291 (1952).

[5]) R. L. REBERTUS, H. A. LAITINEN and J. C. BAILAR, jr., J. Amer. chem. Soc. **75**, 3051 (1953); R. L. REBERTUS, Univ. of Illinois, Urbana, Abs. **14**, 1917, Dissertation 1954, Chem. Abstr. p. 3717 C (1955).

[6]) P. V. GOGORISHVILI, M. V. KARKARASHVILI and L. D. TSITSISHVILI, Chem. Abstr. p. 5616 e (1957); Журнал Неорганической Химии [J. anorg. Chem.] **1**, 1731 (1956); Chem. Abstr. p. 1834 a (1958); Журнал Неорганической Химии [J. anorg. Chem.] **2**, 1040 (1957).

[7]) P. V. GOGRISHVILI and M. G. TSGITISHVILI, Chem. Abstr. p. 7403 d (1960); (Soobsh cheniya Akad. Nank Gruzin S.S.R. **23**, 281 (1959) Georgian).

[8]) K. A. HOFMANN and E. C. MARBURG, Ber. dtsch. chem. Ges. **30**, 2019 (1897).

[9]) CUMMING and KAY, Quantitative Chemical Analysis, IX Edn. p. 160, 1945.

[10]) P. RAY and P. V. SARKAR, J. chem. Soc. Trans. Part I, Vol. CXVII, p. 321 (1920).

[11]) CUNNING and KAY, Quantitative Chemical analysis, X Edn., p. 305, 1945.

[12]) ARTHUR I. VOGEL, A Text Book of Quantitative Inorganic Analysis, II Edn., p. 380, 1951.

[13]) CUMMING and KAY, Quantitative Chemical Analysis, IX Edn., p. 137, 1945.

[14]) W. W. SCOTT, Standard Methods of Chemical Analysis, V Edn., Vol. I, p. 614.

$Zr(SO_4)_2 \cdot 4H_2O$ was dissolved in conductivity water and filtered through a gravimetric filter paper to obtain a clear and almost colourless solution. Zirconium was extimated[15]) as pyrophosphate.

Copper chloride solution was prepared by dissolving pure copper chloride and its strength determined by the usual iodometric method.

Preparation, Properties and Chemical Analysis of the Complexes

The complexes of hydrazine with Cobalt chloride, and copper chloride were prepared by mixing their standard solutions in about 99% alcohol with constant stirring in such a way that hydrazine was in slight excess from the ratio given by the curves of thermometric and conductometric titrations. The hydrazine complexes of cobalt sulphate, Zinc chloride and sulphate, Nickel sulphate and Zirconium sulphate were prepared by mixing their aqueous solutions in the same way. The precipitate in each case was allowed to settle, supernatant liquid decanted and the precipitate transferred to centrifuging tubes with 95% alcohol. It was centrifuged, centrifugate decanted, residue washed with 95% alcohol and this process repeated several times. It was finally washed with absolute alcohol 5—6 times, taken in a china dish and dried in a vacuum desiccator over concentrated sulphuric acid.

If aqueous solutions of hydrazine hydrate and cobalt chloride were mixed, a pink precipitate was obtained, which was partially converted into a blue precipitate. The blue precipitate was washed with water, dried in a vacuum desicator when a green powder was obtained which on analysis was found to be cobalt hydroxide. If the cobalt sulphate hydrazine complex is washed with water and dried in the desiccator, a bright almond coloured complex is obtained whereas the colour of that prepared by washing with alcohol is less deep. If the zinc chloride and sulphate complexes of hydrazine are washed with water, hydrolysis occurs and the whole of hydrazine is washed away.

For the analysis of the complexes, separate amounts of each complex were weighed for the estimation of the metal ion, acid radical and hydrazine. A weighed amount (0.2 gm.) of the complex was dissolved in moderately concentrated nitric acid and the solution heated on water bath for 30 minutes and then used for the estimation of metal ion or the acid radical. Chloride was estimated gravimetrically as silver chloride and sulphate as Barium sulphate. The metal ions were estimated as given under "preparation and standardization of solutions". For the estimation of hydrazine the complex was dissolved in dilute HCl and hydrazine estimated as given earlier.

The Cobalt chloride hydrazine complex is a dark pink powder, insoluble in cold water and organic solvents viz. alcohol, benzene, chloroform, ether, carbon tetrachloride pyridine, etc. Boiling water gives a blue solution, hydrochloric, nitric and sulphuric acids and aqua regia dissolve it.

The Cobalt sulphate-hydrazine complex is bright almond coloured, has no characteristic smell, is insoluble in organic solvents viz. alcohol, ether, chloroform, carbon tetra chloride, acetone, toluene, xylene and dioxane at room temperature as well as higher temperatures, dissolves in dilute mineral acids and gives a clear pink coloured solution with dilute nitric and hydrochloric acids in which cobalt, hydrazine and sulphate can be tested.

[15]) ARTHUR I. VOGEL, A Text Book of Quantitative Inorganic Analysis, II. Edn., p. 476.

The zinc chloride and sulphate complexes of hydrazine are *white powders, insoluble in wather, alcohol and acetone and soluble in* dilute and concentrated common mineral acids.

The nickel hydrazine complex is a beautiful reddish violet compound. If the precipitate of this compound is washed with water, the colour of the compound is darker. The complex is insoluble in water, alcohol, acetone, ether, benzene, carbon tetrachloride and soluble in dilute mineral acids.

The white gelatinous precipitate of zirconium sulphate hydrazine complex on drying becomes white powder which is insoluble in water and common organic solvents but soluble in mineral acids only on heating.

The copper chloride hydrazine complex is blue black in colour, decomposes slowly on exposure to air and gives a turbid solution in cold water, which on boiling deposits an orange red precipitate of cuprous oxide. It is insoluble in common organic solvents but soluble in mineral acids slowly in cold and rapidly on heating

Conductometric Titrations. A special metre bridge (500 cm. manganin wire) was used in conjunction with an oscillator (W. T. W. 1 K cys.), a headphone and a dip type con-

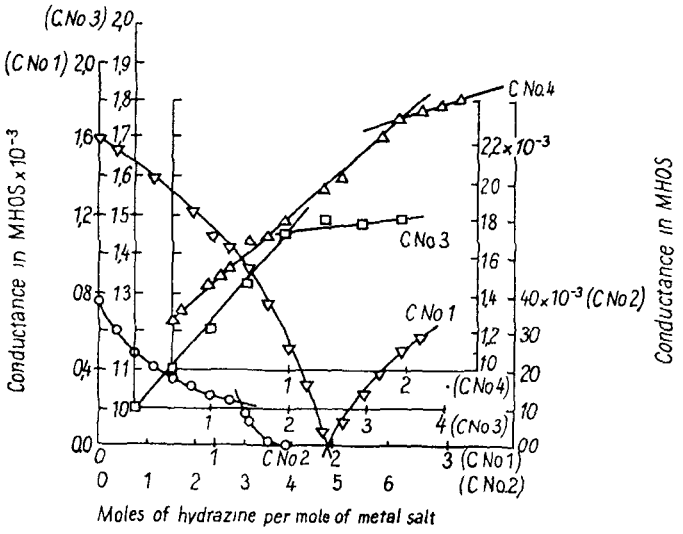

Fig. 1. Conductometric Titrations. C. No 1 Complex with $CoCl_2$, c No 2 Complex with $CoSO_4$, c. No 3 Complex with $ZnCl_2$, c. No 4 Complex with $ZnSO_4$

ductivity cell Both direct and reverse titrations were performed and volume correction applied wherever required (Fig. 1 and 2)

Thermometric Titrations A DEWAR's flask of 100 ml capacity housed in a metal enclosure and covered with felt was used. The annular space between the flask and the

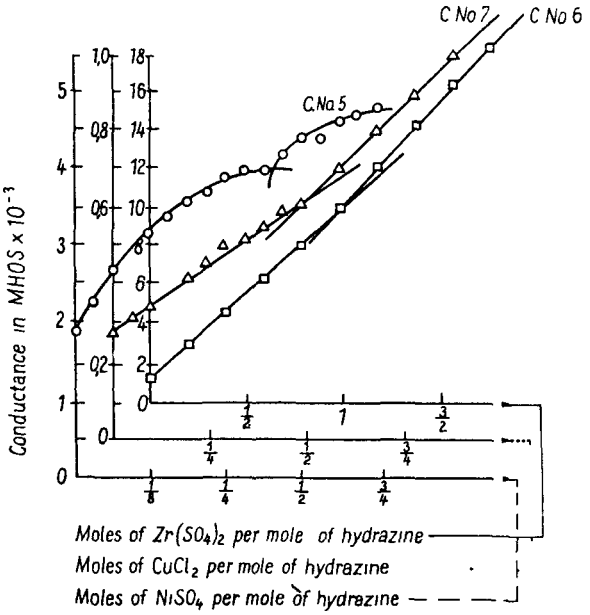

Fig. 2. Conductometric Titrations

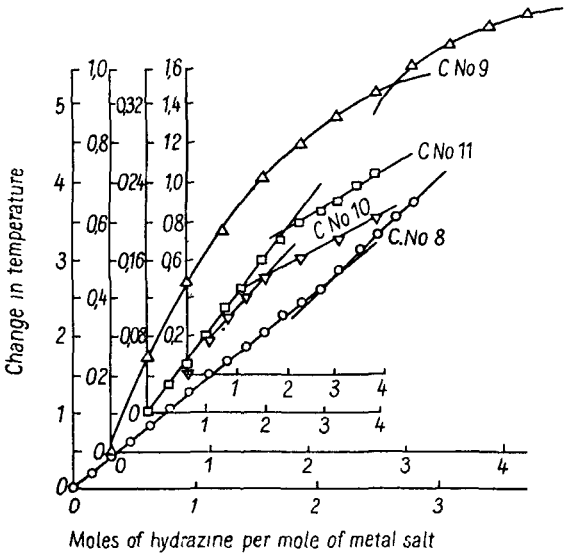

Fig 3. Thermometric Titrations C No 8 Complex with $CoCl_2$, c. N. 9 Complex with $CoSO_4$, c. No. 10 Complex with $ZnCl_2$, c. No. 11 Complex with $ZnSO_4$

vessel was packed with glass wool. The burette was wrapped with asbestos on all sides except for the streak left to make the graduations visible. The reactants were kept for sometime to attain room temperature before actually starting the titrations. Variations in temperature were noted by a BECKMAN thermometer which was previously set at room temperature. Both direct and reverse titrations were performed (Fig. 3 and 4).

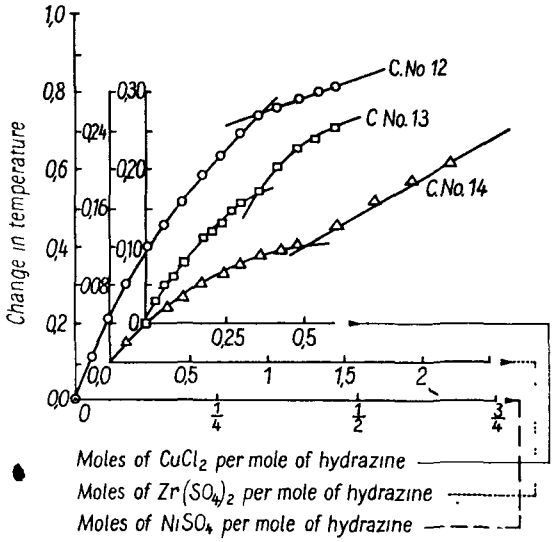

Fig. 4. Thermometric Titrations

Results and Discussion

Chemical Analysis

1. Cobalt Chloride Hydrazine Complex
Co 30.3%; Cl 36.33%; N_2H_4 32.22%; Total 98.85%; Formula: $Co_{1.028}\,Cl_{2.01}\,(N_2H_4)_2$.

2. Cobalt Sulphate Hydrazine Complex
CO 23%; SO_4 38.4%; N_2H_4 34.6%; Total 96.0%; Formula: $Co(SO_4)_{1.02}\,(N_2H_4)_{2.77}$.

3. Zinc Chloride Hydrazine Complex
Zn 31.41%; Cl 32.6%; N_2H_4 29.65%; Total.93.66%; Formula: $ZnCl_{1.91}\,(N_2H_4)_{1.93}$.

4. Zinc sulphate Hydrazine Complex
Zn 29.30%; SO_4 42.91%; N_2H_4 24.20%; Total 95.41%; Formula: $Zn(SO_4)\,(N_2H_4)_{1.69}$.

5. Nickel Sulphate Hydrazine Complex
Ni 23.05%; SO_4 38.19%; N_2H_4 37.23%; Total 98.47%; Formula: $NiSO_4 \cdot (N_2H_4)_{2.97}$.

6. Zirconium Sulphate Hydrazine Complex
Zr 40.17%; SO_4 42.18%; N_2H_4 13.92%; Total 96.27%; Formula: $ZrSO_4 \cdot (N_2H_4)_{0.99}$.

7. Copper Chloride Hydrazine Complex
Cu 33.02%; Cl 36.85%; N_2H_4 30.89%; Total 100.76%; Formula: $CuCl_{1.98} \cdot (N_2H_4)_{1.799}$.

The results of chemical analysis, conductometric and thermometric titrations give the following formulae for the various complexes studied.

$Co(N_2H_4)_2Cl_2$, $Co(N_2H_4)_3SO_4$, $Zn(N_2H_4)_2Cl_2$, $Zn(N_2H_4)_2SO_4$, $Ni(N_2H_4)_3SO_4$ and $Cu(N_2H_4)_2Cl_2$.

In dihydrazinate of cobalt chloride, the cobalt ion is hexacoordinated and not four coordinated because $CoCl_2 \cdot 2N_2H_4$ seems to be non-ionic as the conductance tends to become zero at inflextion point in the curve of conductometric titration (vide Fig. 1, Curve 1).

a.

In aqueous solution, $Zr(SO_4)_2$ behaves as if it were zirconylhydrosulphate $ZrOSO_4 \cdot H_2SO_4$ or $ZrO(HSO_4)_2$ i. e. in aqueous medium ZrO^{++} ions should be present and hence according to conductometric and thermometric titrations the metal hydrazine ratio of 1:1 may be interpreted by hydrolysis of $Zr(SO_4)_2$ to $ZrOSO_4$ and

$$ZrOSO_4 + N_2H_4 \rightarrow ZrON_2H_4 \cdot SO_4.$$

The results of chemical analysis are not in accordance with this formula although the total percentage does not come exactly to 100. However chemical analysis gives the formula $ZrSO_4 \cdot N_2H_4$. Further work on this subject is in progress.

Aligarh (India), Aligarh Muslim University, Department of Chemistry.

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Physico-Chemical Studies on the Titanium(III)-Chloride-2-2'-dipyridyl Complex

By M. Tariq Siddiqui, Naseer Ahmad and S. M. F. Rahman

With 2 Figures

Summary

Titanium(III) chloride was found to undergo complex formation with 2.2′-dipyridyl producing a white crystalline compound The composition of the complex in solution was found to be in the molar ratio of 1:2 (titanium·dipyridyl) by conductometric and potentiometric titrations The complex was also recrystallised, and its analysis confirmed the results of the titrations The complex was found to yield a single free chloride ion in solution A possible structure of the complex is proposed

Inhaltsübersicht

$TiCl_3$ bildet mit 2,2′-Dipyridyl einen 1·2 Komplex, der in Substanz isoliert und konduktometrisch, potentiometrisch sowie analytisch untersucht wurde Auf Grund der Beobachtung, daß nur eines der drei Chloratome in wäßriger Lösung als Cl^- abdissoziert, wird ein Strukturvorschlag gemacht.

The chemical literature abounds with the complexes of dipyridyl HERZOG and TAUBE[1]) studied the complexes of titanium(0) and titanium(I) with dipyridyl and ortho-phenanthroline This paper deals with studies of the titanium(III)-chloride-2,2′-dipyridyl complex. When crystals of pure titanium(III) chloride are mixed with solid dipyridyl and moistened with a drop of water or alcohol, the colour changes from violet to green, blue, and later on to light pink (on drying in a vacuum desiccator) take place. The dried light pink mass was dissolved in water and left in a vacuum desiccator for slow evaporation. Beautiful colourless crystals were obtained (No complex formation occured with titanium(IV) chloride under these conditions) The complex was chemically analysed for chlorine and titanium and was also studied employing potentiometric and conductometric titrations. The number of coordinated chlorine atoms were also evaluated.

[1]) S. HERZOG and R. TAUBE, Z. anorg. allg. Chem. **306**, 159 (1960)

Experimental

Standard solution of Ti(III) chloride[2]) was prepared by dissolving $TiCl_3 \cdot 3\,H_2O$ [3]) in air-free doubly distilled water. 0.3123 gm of dipyridyl (E. MERCK) was dissolved in air free doubly distilled water to which a drop of pure diluted. HCl had been added to obtain 100 ml of a 0.2 M solution.

Potentiometric titrations were performed by taking a known volume of standard Ti(III) chloride solution containing a trace of titanium(IV)-chloride in a beaker in which were dipped a platinum and a calomel electrode adding then dipyridyl from the burette. A Tinsley potentiometer with a lamp and scale outfit was used for finding out the changes in E. M. F. (Fig. 1).

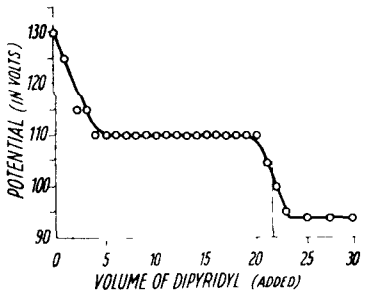


Fig. 1. Potentiometric titration Dipyridyl 0.04 M, 20 ml of 0.02 M $TiCl_3$

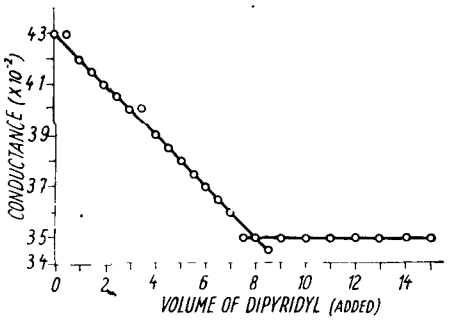


Fig. 2. Conductometric titration Dipyridyl 0.02 M 40 ml of 0.2 M $TiCl_3$

Conductometric titrations were performed using a conductivity bridge and a head phone to detect the null point (Fig. 2).

The standard solutions of the two reagents of 0.02 M strength were mixed in the ratio of 1:2 (titanium:dipyridyl) in a porcelain dish and allowed to evaporate slowly in a vacuum desiccator. Colourless crystals were obtained in a week's time. 0.2 gm of the complex was weighed in a previously weighed platinum crucible and fused with $NaHSO_4$. The fused mass was dissolved in very dilute hydrochloric acid and titanium estimated gravimetrically[4]). For the estimation of chlorine as AgCl, the complex was dissolved in moderaely concentrated nirtic acid and boiled for about 10 minutes prior to the addition of silver nitrate.

Results of Chemical analysis: Observed amount of Ti 10.2%; Cl 22.7%. Calculated for $TiCl_3 \cdot 2$ dipyridyl: Ti 10.3%; Cl 22.8%.

For ascertaining the number of chlorine atoms bound with the central metal ion by coordinate bonds, a weighed amount of the complex was dissolved in doubly distilled air-free water. Silver nitrate solution was added in excess and after waiting for about 3 minutes, it was filtered through a weighed sintered glass crucible. The weight of AgCl was determined and the number of chlorine atoms in the complex found out. These chlorine atoms were taken to be ionizable. Observed chlorine: 7.643%; Calculated for one chloride radical: 7.63%.

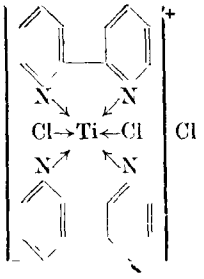
[2]) A Text Book of Quantitative Inorganic Analysis by A. I. VOGEL, II Ed., Longmans, Green and Co., 1955, p. 316.

[3]) MELLOR, Inorganic and Theoretical Chemistry, Vol. VII, p. 74.

[4]) SCOTT, Standard Methods of Analysis, Vol. I, V. Ed. 1939, p. 983.

Discussion

The potentiometric and conductometric titrations give the molar ratio of 1:2 (Ti(III) chloride:dipyridyl). This was confirmed by chemical analysis. Since it was found that conductance decreases in the formation of the complex (curve No. 2), it was possible to think that a few chloride ions of titanium(III) chloride got bound with titanium. It was found that immediate precipitation of only one chlorine atom per molecule of the complex takes place by the addition of silver nitrate. Hence the structure of the complex may be:



The authors are indebted to Prof. A. R. KIDWAI, Head, Department of Chemistry, Aligarh Muslim University, Aligarh, for providing facilities to carry out these investigations.

Aligarh (India), Department of Chemistry, Aligarh Muslim University.

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Spectrophotometric Studies on the Complexes of Titanium (III) with Cacotheline, Alizarin & Dithizone

S M S AKHTAR, NASEER AHMAD & S M F RAHMAN
Department of Chemistry, Aligarh Muslim University, Aligarh

Manuscript received 16 *January* 1964

Titanium (III) chloride forms a reddish brown complex with cacotheline, an intense red complex with alizarin and an intense green complex with dithizone which show absorption maxima at 400, 435 and 435, and 595 mμ respectively. Lambert and Beer's law is found to hold good for cacotheline, alizarin and dithizone complexes in the concentration ranges 0.1625×10^{-4} to $0.25 \times 10^{-3}M$, 0.44×10^{-4} to $0.2886 \times 10^{-3}M$ and 0.1333×10^{-4} to $0.1133 \times 10^{-3}M$ respectively. The composition of the three complexes, determined by Job's method, slope and mole ratio methods is found to be 1 : 3 (metal : ligand). Titanium also forms insoluble complexes with cacotheline and alizarin in the ratio 1 : 1. Tentative structures have been proposed for the titanium complexes with alizarin and dithizone.

CACOTHELINE[1-7], alizarin[8-23] and dithizone[24-27] have been extensively used for the detection and estimation of a number of anions and cations. The complexes of these reagents with a number of metals have also been reported in literature. Lang[1] reported that strong reducing agents, e.g. titanium (III) chloride reduce cacotheline to a violet coloured compound. He extended the use of cacotheline in the detection of thiosulphate, copper, iron, formaldehyde, etc. Ribby and Gantz[2] employed cacotheline for the spectrophotometric determination of tin. Cacotheline has been used for the detection of Fe (II), and Fe (III)[3] and Cu (II)[4]. It has also been used as an oxidation-reduction indicator[5] in the titrations of Sn^{2+}, Fe^{3+}, $Cr_2O_7^{2-}$, IO_3^-, VO_3^- $Fe(CN)_6^{3-}$, Ce^{4+} and elemental iodine. Recently Szarvas and Lantos[6] used cacotheline in stannometric titrations, drew oxidation-reduction potential-colour change curves of the indicator and measured the apparent standard oxidation-reduction potential. Bognar[7] used it in conjunction with hydrazine in the determination of molybdenum

The chemical literature abounds with the complexes of alizarin. Atack[8] was the first to propose the formation of a lake with alizarin as a confirmatory test for aluminium. Complexes of alizarin with Cr[9], Cu, Cd, Fe and Ni[10,11], Co[12], Bi[13], Al[14] In[15] and Ca[16] have been reported. The lakes of alizarin were previously regarded as absorption complexes[17] but Babko and Nazarchuk[18] have asserted that under conditions of colorimetric measurements, metal ions form definite chemical compounds with alizarin. Many complexes of alizarin are salts rather than coordination compounds[19-21]. Ugulava[22] used zirconium reagent for the colorimetric determination of fluorine. Quite recently Pasternak[23] studied the coprecipitation of plutonium with alizarin.

The complexes of dithizone with a large number of metal ions have been studied. Its use in the

solvent extraction of elements has been reviewed by Freiser[24] Bazhanova and Busev[25] have reported the colour of the inner complexes of bismuth with dithizone Henderson and Snyder[26] have reported a rapid spectrophotometric determination of lead and its alkyl compounds Bryan and Knope[27] have determined the configuration of cupric dithizonate

A review of the literature reveals that titanium complexes with cacotheline, alizarin, and dithizone have not been studied so far. It was, therefore, considered of interest to study the titanium (III) complexes with these reagents The results of this investigation are reported in this communication

Titanium (III) chloride forms a reddish brown complex with cacotheline, an intense red complex with alizarin and an intense green complex with dithizone. The insoluble complexes of cacotheline and alizarin isolated by adding acetone to the solution of their soluble complexes have been chemically analysed for titanium.

Materials and Methods

Reagents and standard solutions — Titanium (III) chloride[28] was dissolved in air-free double distilled water and the strength of the solution was determined by titrating against potassium permanganate[29] Since titanium (III) chloride is apt to hydrolyse and undergo atmospheric oxidation, fresh solutions were always prepared immediately before use and kept covered with a layer of kerosene oil

Cacotheline (E Merck) (0·122 g) was dissolved in 250 ml of air free double distilled water to obtain 0 01*M* solution It was stored in a well stoppered flask wrapped with black paper Alizarin (E Merck) (0 6 g) was dissolved in 100 ml of 98 per cent alcohol by warming on a water bath and the solution made 250 ml to obtain 0 01*M* solution Dithizone (BDH) (0 1281 g) was dissolved in 98 per cent alcohol by warming on a water bath It was cooled and made up to 500 ml to obtain 0 01*M* solution

Absorption maxima of the complexes were determined by Vosburgh and Cooper method[30] Optical densities of 0 1 $10^{-2}M$ solutions of titanium (III) chloride and complexing agent and their mixtures in the ratio of 1 1, 1 2, 1 3, 2 1 and 3 1 were measured with Bausch & Lomb Spectronic-20 colorimeter at wavelengths in the visible range The absorption maxima for cacotheline and its complex occurred at 400 mμ and that for alizarin and its complex at 435 mμ For dithizone the λ_{max} were at 425 and 595 mμ whereas for the complex these were at 435 and 595 mμ

Lambert and Beer's law was found to hold good for cacotheline, alizarin and dithizone complexes at the concentration range $0\,1625\times10^{-4}$ to $0\,25\ 10^{-3}M$, $0\,44\ 10^{-4}$ to $0\,2886\times10^{-3}M$ and $0\,1333\times10^{-4}$ to $0\,1133\times10^{-3}M$ respectively

Results

The composition of the complexes formed was determined by the following methods

Job's method[31] — Solutions of titanium (III) chloride and the complexing agent were mixed in different ratios and their optical densities determined at the corresponding maxima The optical densities for the same concentrations of the complexing agents were also determined and the difference plotted against the composition of the mixture Titanium (III) chloride at low concentrations becomes colourless and shows negligible absorption In the case of dithizone, the measurements were made at 595 mμ also (Fig 1)

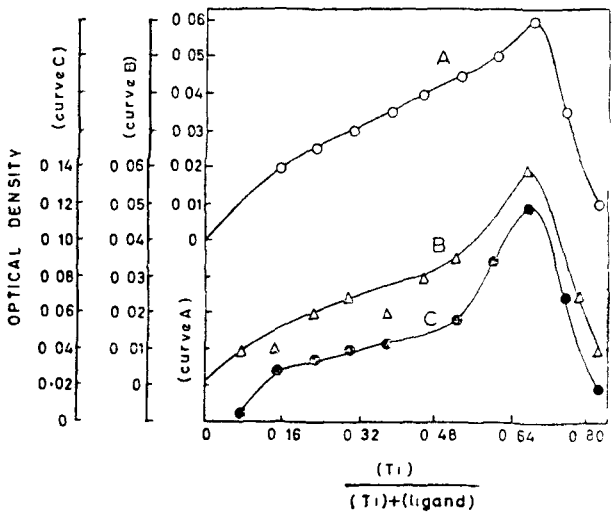


Fig 1 Composition of the complexes of titanium (III) with (A) dithizone (conc $0\,333\times10^{-3}M$) (B) cacotheline (conc $0\,22\times10^{-3}M$) and (C) alizarin (conc $0\,25\times10^{-3}M$) using Job's method

Molar ratio method[32] — Titanium (III) chloride solution (2 ml) was taken in 12 test tubes separately to which varying volumes of cacotheline of the same concentration were added and the total volume made 12 ml by adding requisite amount of water In another set of 12 test tubes, the same volumes of cacotheline of the same concentration were taken and the final volume made 12 ml with water The optical densities were determined and the difference plotted against the volume of cacotheline

In another set, to the constant volume of cacotheline varying volumes of titanium (III) chloride were added and the optical densities of these mixtures were plotted against the volumes of titanium (III) chloride (Fig 2)

Slope ratio method — Titanium (III) chloride solution (4 ml) was taken in 12 test tubes separately and the varying volumes of the complexing agent added making the total volume constant, i.e. 12 ml by adding water Similarly in 12 test tubes 4 ml of complexing agent was taken and varying volumes of titanium (III) chloride added keeping the total volume constant as above The optical densities were measured and plotted against the volume of the reagent which had been kept variable The ratio of the slopes of the two lines is the ratio between the two reactants (Fig 3)

Effect of pH — A solution (2 ml) containing titanium (III) chloride and cacotheline (in the ratio of 1 3) was mixed with 10 ml of buffer solutions having different *p*H values and then

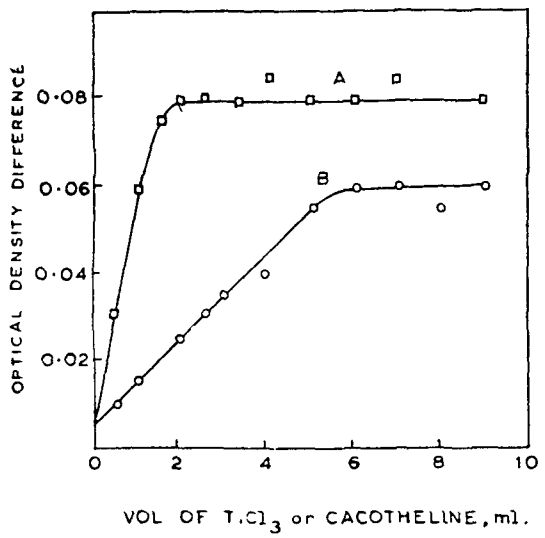


Fig 2 — Composition of titanium (III) cacothelline complex by molar ratio method [(A) To $M/1000$ cacothelline (3 ml) was added $M/2000$ $TiCl_3$ solution, and (B) to $M/1500$ $TiCl_3$ (2 ml) was added $M/1500$ cacothelline]

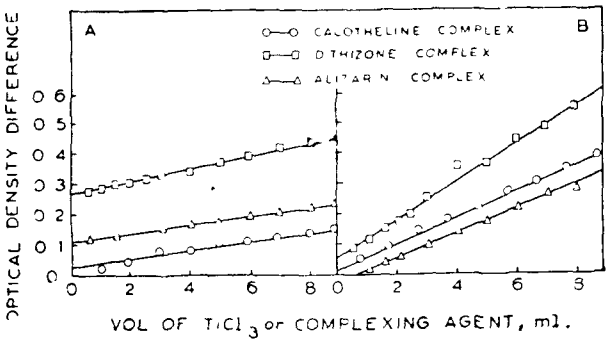


Fig 3 — Composition of the complexes of titanium (III) with cacothelline dithizone and alizarin using slope ratio method [(A) Varying the amount of $TiCl_3$, and (B) of complexing agent]

optical densities noted at different wavelengths (Fig. 4).

Preparation and analysis of the insoluble complexes — To the reddish violet solution obtained by mixing titanium (III) chloride and cacothelline in the ratio 1 3, acetone was added and the precipitate obtained was washed with acetone and dried in a vacuum desiccator over concentrated sulphuric acid. The dried complex was reddish violet in colour and soluble in mineral acids. Titanium (III) chloride and alizarin were mixed in the molar ratio 1 3 in alcohol, and acetone added when a red powder was obtained. It was also dried in a vacuum desiccator over concentrated sulphuric acid. It was insoluble in hot water, alcohol, ether and dilute mineral acids. No such complex could be isolated in the case of dithizone.

A weighed quantity of the dried complex was fused with potassium hydrogen sulphate in a platinum crucible, the fused mass dissolved in dilute hydrochloric acid and titanium estimated gravimetrically[33]. The two complexes were found

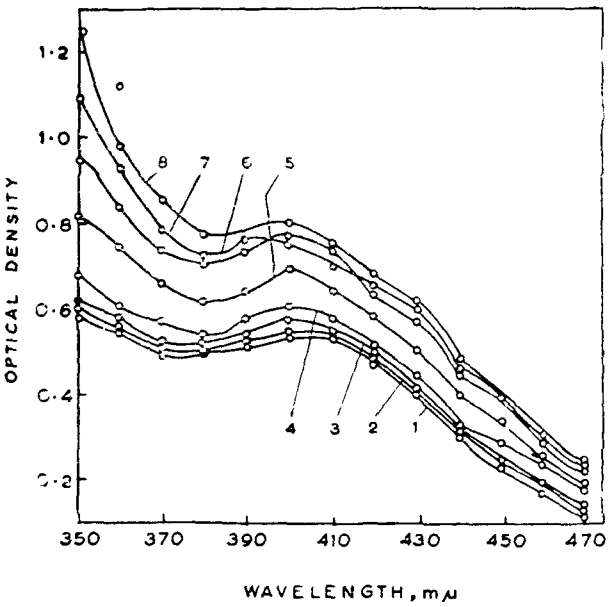


Fig 4 — Effect of varying *p*H on titanium (III) cacothelline complex [(1) 2 3, (2) 3 0, (3) 4 2, (4) 6 8, (5) 7 0, (6) 8 0 (7) 9 2, and (8) 11 5]

Table 1 — Analysis of the Insoluble Titanium Complexes with Cacothelline and Alizarin

Complex	Titanium %	Ligand (by difference) %	Ratio (metal : ligand)
Ti-cacothelline	8 92	91 08	1 : 1 14
Ti-alizarin	17 75	82 25	1 : 1

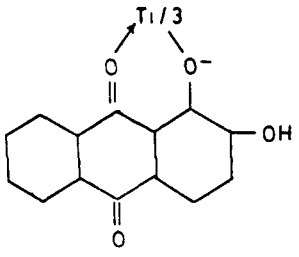
to be free from chlorine. The results of analysis are given in Table 1.

Discussion

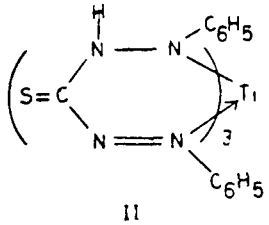
Job's method, molar ratio and slope ratio methods give the molar ratio 1 : 3 for titanium-cacothelline complex. There is no shift in the absorption maxima of the complex with variation in *p*H. The insoluble complex on analysis gives the ratio 1 : 1 for the two reactants.

The ratio of 1 : 3 (titanium alizarin) emerge for this complex in alcoholic medium. Since the medium was alcoholic and on the acidic side it is quite probable that only one of the two OH groups ionizes and then coordination with one doubly bonded oxygen occurs. The structure (I) may be assigned to the titanium-alizarin complex.

Two types of complexes may be formed when a metal ion combines with dithizone, a complex containing the bidentate keto form of dithizone and the other containing a tridentate enol form of the ligand entailing replacement of both hydrogen atoms from the hydrazide function. But since the formation of enol species[31] takes place only in basic solution, the possibility of a tridentate appears to be very little in view of the fact that the products were obtained in the acidic medium. Therefore, a



I



II

complex with the keto form of dithizone is possible in which one hydrogen is displaced from the imido group and the ligand behaves as a bidentate The Job's method and slope ratio method give a ratio 1 3 (titanium dithizone) From this ratio it may be concluded that a six-membered ring is formed and an inner complex results as shown in structure (II) for this complex

Acknowledgement

Authors' thanks are due to Prof A R Kidwai for providing facilities to carry out these investigations

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Spectrophotometric Studies on the Complexes of Eriochrome Black-T with Titanium (III & IV)

S. M. S. Akhtar, Naseer Ahmad, and S. M. F. Rahman

Eriochrome Black T(H_3L) exists in three differently coloured species in solution[1] and the equilibria between the three species are

$$\underset{\text{Wine-red}}{H_2L^-} \xrightarrow{k\ 6.3} \underset{\text{Blue}}{HL^{2-}} \xrightarrow{k\ 11.5} \underset{\text{Orange}}{L^{3-}}$$

Eriochrome Black-T produces a green coloured complex with titanium(III) in aqueous and with titanium (IV) in ethanolic media

Procedure—Titanium (III) chloride solution was prepared from $TiCl_3\ 6H_2O$ crystals and standardised Titanium (IV) chloride ($TiCl_4$, 12% w/v soln containing 15% HCl, B D H) was used for preparing its solution and standardised $0.2\times10^{-2}M$ of Eriochrome Black T was prepared in air-free double distilled water or in 98% ethanol

The wave length maxima were ascertained for the dye and the mixtures of the dye and the metal salts according to Vosburgh and Cooper's method[2]. It was found to be 525 mμ for the dye and for its titanium (III) complex in aqueous medium, the λ_{max} was 525mμ at *p*H 3.0 to 6.4, 565mμ at *p*H 7.1 to 10.1, and 550 mμ at *p*H 11.5. The absorption maximum for titanium (IV) complex in ethanolic medium lies at 530 mμ and 600 mμ.

The composition of the titanium(III) dye complex (using $0.1\times10^{-2}M$ aqueous solutions) was 1:3 (metal : ligand) by Job's method of continued variations[3] and also by the mole ratio and slope ratio methods[4].

The interaction of titanium(III) chloride and the dye was studied in buffer solutions of *p*H 4.2, 7.2, 9.0, and 12.0 and the ratios of 1:3, 1:2, 1:2, and 1:1 titanium dye respectively, were found out, showing other complexes also, which can be represented by the following empirical formulas

At *p*H 4.2 $\quad Ti^{3+} + 3H_2L^- \longrightarrow Ti(H_2L)_3$

At *p*H 7.0 and 9.0 $\quad Ti^{3+} + 2HL^- \longrightarrow Ti(HL)_2^-$

At *p*H 12.0 $\quad Ti^{3+} + L^{3-} \longrightarrow Ti\,L$

1. Martell and Calvin, 'Chemistry of Metal Chelate Compounds', 1959, p. 486, Prentice Hall Inc. N.Y.
2. *J. Amer. Chem. Soc.*, 1941, **63**, 437
3. *Compt. rend.*, 1925, **180**, 928
4. Harvey and Manning, *J. Amer. Chem. Soc.*, 1950, **72**, 4488

To $0.2\times10^{-2}M$ solution (300 ml) of Eriochrome Black-T was added dropwise titanium(III) chloride ($0.2\times10^{-2}M$, 200 ml), when a reddish brown flocculent precipitate appeared. It was washed with water and dried in a vacuum desiccator (H_2SO_4). The dried product was brownish green in colour. The complex was found to be free of chloride.

It was fused with fusion mixture in a platinum crucible. The fused mass was dissolved in HCl (dil.) and titanium was determined as hydroxide and sulphur, as barium sulphate.

The results indicated a ratio of 2:3 (metal: dye) and the interaction therefore can be represented by the equation:

$$2\ Ti^{3+} + 3\ HL^{2-} \longrightarrow Ti_2\ (HL)_3$$

The titanium (IV) complex with the dye was studied by the three methods. stated above, in ethanolic media at 530 mμ and 600mμ and the ratio found was 1:2 (metal: dye).

The authors are thankful to Prof. A. R. Kidwai for providing facilities to carry out these investigations.

Department of Chemistry,
Aligarh Muslim University,
Aligarh.

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SPECTROPHOTOMETRIC STUDIES ON THE TITANIUM (III) CHLORIDE-*P*-NITROBENZENE AZOCHROMOTROPIC ACID COMPLEX

M. MAHFOOZ KHAN *and* NASEER AHMAD

NATIONAL ACADEMY OF SCIENCES, INDIA
ALLAHABAD

SPECTROPHOTOMETRIC STUDIES ON THE TITANIUM (III) CHLORIDE-*P*-NITROBENZENE AZOCHROMOTROPIC ACID COMPLEX

By

M. MAHFOOZ KHAN *and* NASEER AHMAD

Department of Chemistry, Aligarh Muslim University, Aligarh

[Received on 18th March, 1965]

ABSTRACT

Chromotrope 2B gives a pink coloured solution in water and forms a less pink complex with Titanium (III) chloride. The λ max for the ligand as well as the complex is 520 mμ. Beer and Lambert's Law is found to hold good at the concentration range of $0{\cdot}375\times10^{-3}$ — $0{\cdot}5\times10^{-4}$M. Job's method of continued variations in aqueous solution and in neutral pH buffer yields a molar ratio of 1 : 2 (Titanium (III) chloride : Chromotrope 2B) The same ratio emerges from molar-ratio method. The complex is stable between pH range of 2 to 9 while above this range precipitation occurs on keeping for sometime. A structure for the complex has been proposed

Chromotropic acid is well known for its chelating properties and has been extensively studied. Comparatively very little work has been done on metal chelates of *p*-nitrobenzene azochromotropic acid (sodium salt) known as chromotrope 2B (abbreviated in this paper as CTB). Titanium (III) chloride forms a complex with chromotrope 2B, which is less pink than the chelating agent itself. The present communication deals with our spectrophotometric studies on this complex.

EXPERIMENTAL

Aqueous solution of titanium (III) chloride was prepared by dissolving crystals[1] of $TiCl_3.6H_2O$ in air free double distilled water and standardised.[2] Always fresh solutions were prepared before use and kept covered with a layer of kerosene oil throughout the investigations. B. D. H. reagent grade chromotrope 2B was used for preparing its solution.

For spectrophotometric measurements Bausch and Lomb spectronic –20 was used. Titanium (III) chloride and chromotrope 2B were mixed in the molar ratio of 1 : 1, 1 : 2 and 2 : 1 and solutions of different concentrations were prepared by diluting with air free double distilled water, to verify the applicability of Beer and Lambert's Law. It was found to hold good for the concentration range of $0{\cdot}375\times10^{-3}$ to $0{\cdot}5\times10^{-4}$M for 1 : 2 complex.

The method of Vosburgh and Cooper[3] was employed to ascertain the nature of complexes formed in aqueous solution. $0{\cdot}5\times10^{-4}$M solutions of titanium (III) chloride and chromotrope 2B were mixed in the ratio of 1 : 1, 1 : 2, 1 : 3, 2 : 1 and 0 : 1 and their absorbance was determined at different wave lengths in the visible range. The λ max. for the complex as well as chromotrope 2B is 520 mμ (Fig. 1).

$0{\cdot}8\times10^{-4}$M and $0{\cdot}6\times10^{-4}$M aqueous solutions of titanium (III) chloride and chromotrope 2B were mixed according to Job's method of continued variations[4] for two sets, their optical densities noted at 520 mμ and the 'Y' plotted against the composition of the mixture (Fig. 2).

FIG NO 1

VOSBURGH AND COOPER METHOD

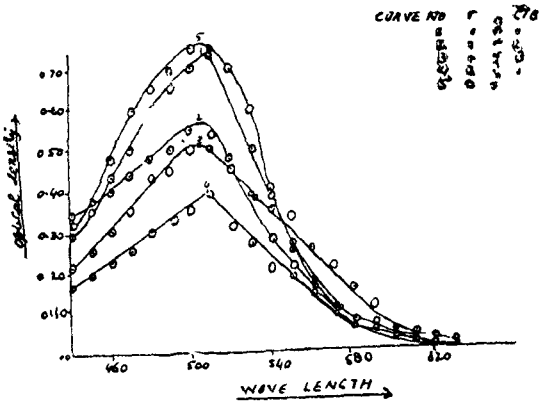


FIG-NO.2

JOBS METHOD

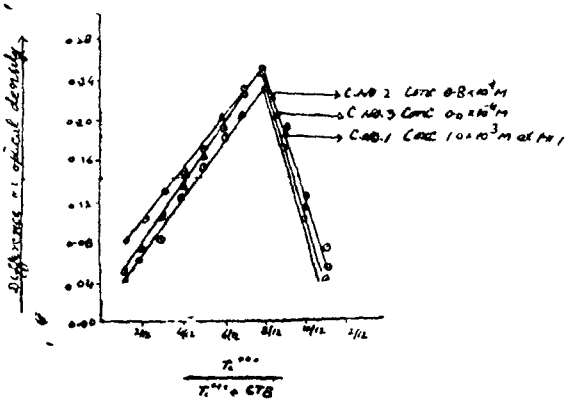


FIG NO 3

MOLAR RATIO METHOD

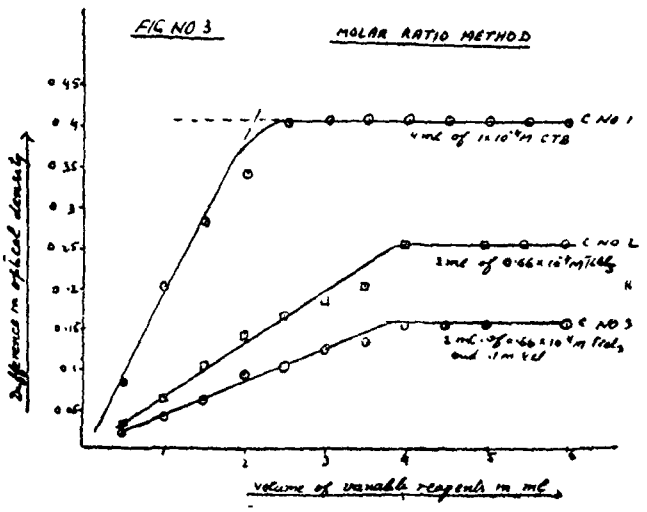
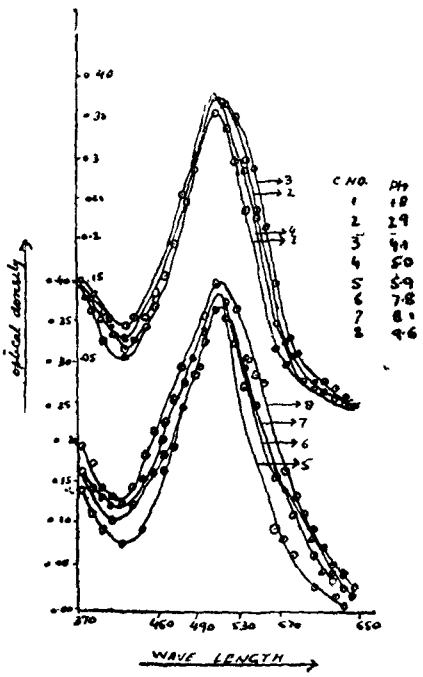


FIG.NO 4

EFFECT OF PH



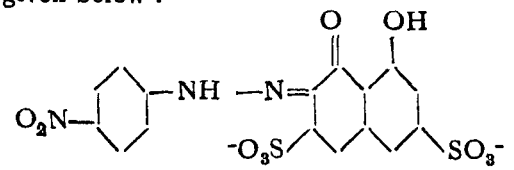
Molar ratio method[5] was also employed to ascertain the composition of the complex. In one set of experiments, the quantity of titanium (III) chloride was kept constant and that of chromotrope 2B was varied and in another set, the quantity of chromotrope 2B was constant and that of titanium (III) chloride was varied (Fig. 3).

To determine the effect of pH on the formation of the complex, equimolecular solutions (1×10^{-3}M) of the reactants were mixed in the ratio of 1 . 2 (metal ligand) and then ten times diluted with buffer mixtures of pH values from 2 to 9. Above pH 9, precipitation occurs on keeping for sometime. The optical densities were determined at different wave lengths in the visible range. It was found that maximum absorption occurs at 520 $m\mu$ at all pH values. (Fig 4).

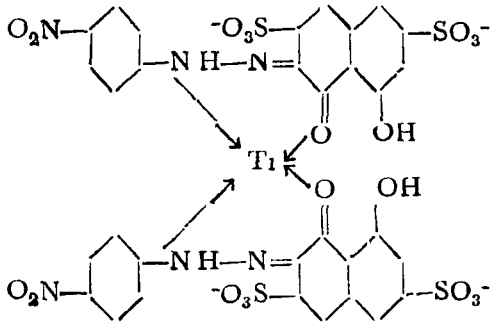
The complex was studied at neutral pH buffer by Job's method (Fig. 2) and at constant ionic strength of 0·1M KCl by molar ratio method (Fig 3).

DISCUSSION

Job's method in aqueous solution and in neutral pH buffer gives the molar ratio of 1 : 2 for titanium (III) chloride and chromotrope 2B. This ratio is confirmed by molar ratio method performed in aqueous solution and at constant ionic strength. Sommer *et al*,[6] suggested that chromotrope 2B in aqueous solution and in acidic medium (0·1N H_2SO_4) displays maximum absorption at 517 $m\mu$ and exists in the form given below :



Since in our case the medium was neutral, the following structure may be suggested for the chelate.



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9

1 : 10 Phenanthroline Complexes of Titanium(III) and Vanadium(IV)

Mohd Mahfooz KHAN and Naseer AHMAD

Department of Chemistry, Aligarh Muslim University, Aligarh, U P, India

(Received February 18, 1966)

Chemical literature abounds with studies of metal complexes of phenanthroline To cite a few, Clark[1] studied complexes with $TiOCl_2$ and VOCl and ascertained a ratio of 1 1 (metal phen where phen=orthophenanthroline) for the two complexes, Herzog and Gramm[2] prepared $V(phen)_3$ and $V(phen)_3I_2$, Trujillo and Brito[3] determined the equilibrium constants of the vanadium IV) phenanthroline complex to be 5 47 and 4 22, and Schaeffer[4] used the formation of a blue coloured vanadium II phenanthroline complex as an end-point indicator in the titration of vanadyl compounds with chromium II) chloride

Orthophenanthroline forms light-slate-coloured and yellowish-white complexes with vanadyl sulphate and titanium(III) chloride respectively, these complexes are little mentioned in the existing chemical literature These complexes were isolated analysed, their magnetic susceptibilities measured and their infrared spectra taken

Experimental

Standard solutions of orthophenanthroline (E Merck) vanadyl sulphate[5] (B D H) and titanium(III) chloride (crystallized $TiCl_3 6H_2O$[6]) were prepared in air-free, doubly-distilled water Solutions of ortho phenanthroline and metal salt were mixed in the molar ratio of 1 2 (metal phen The precipitates were then separated by centrifugation washed repeatedly with tetrahydrofuran dried in a vaccum desiccator over quick lime and analysed

Found V, 14 03 SO_4, 2 09 C 42 9, H, 3 16, N 7 79% Calcd for $VOSO_4$ phen) V 14 85 SO_4, 27 99 C, 41 98 H 2 33 N 8 16

Found Ti, 8 5 Cl 19 [illegible] C [illegible]9 H 4 33

1) R J H Clark *J Chem Soc* **1963** 13[illegible]

2) S Herzog and U Gramm *Z Chem* **4** 32 1964

3) R Trujillo and J Brito *Inst Nucl Chem Phys Quim*, **53B** 249 (1[illegible] *Chem Abstr* **53** 21343 (1959

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5) Quantitative Chemical Analysis, V C Cumenard's Key Index of Chemical Analysis p 367 1948 p 367

6) M Mahfooz S M F Rahman and W U Malik *J Indian Chem Soc* **40** 1[illegible] 1963

N 10 7% Calcd for $TiCl_3$(phen) Ti, 9 31, Cl, 20 7, C, 35 93, H, 3 11, N, 10 88%

Both the complexes are water-soluble, but neither could be crystallised from its aqueous solution since both underwent hydrolysis The densities of the vanadyl complex and the titanous complex are 1 639 g/cc and 1 368 g cc respectively

The $VOSO_4$(phen) complex is paramagnetic with a molar susceptibility of 999 3 / 10 The susceptibility of the complex after the correction for the diamagnetism of the ligand (128×10^{-6}) has been applied is 1 46 B M The titanium(III) complex is only slightly paramagnetic, having a corrected susceptibility of 0 3728 B M

The infrared spectra were taken in Nujol with a NaCl prism and in perfluorocarbon oil with a fluoro ube in the appropriate ranges in order to obviate the spectral peaks of the solvents (Figs 1a and 1b In the $TiCl_3$(phen) complex, significant peaks were observed at 720, 780, 850, 890, 1140, 1180, 1370, 1425, 1480, 1500 1600 3100, and 3350 cm^{-1} In the $VOSO_4$(phen) complex, important peaks were observed at 720 850 980, 1040 1430, 1512, and 1660 cm^{-1}

Discussion

The magnetic susceptibility of the vanadyl complex is 1 46 B M This may be considered to be a proof for the presence of a single unpaired electron in the vanadyl sulphate complex although crystalline $VOSO_4 5H_2O$ possesses a value of 1 73 B M[7] The low value cannot be explained The titanous complex is only slightly paramagnetic although a value of about 1 73 B M was expected Probably the titanous in the complex is so active that oxidised to titanic with ageing

The out-of-plane H-deformation vibrations of phenanthroline at 734 and 841 cm^{-1} are modified on coordination

Phenanthroline	850 841 734	
$TiCl_3$(phen)	720 780 850 890 1140 1180	
$VOSO_4$(phen)	720 850 [illegible]	
1040		
Assignment	C H out-of-plane Deformation vibrations	in-plane H Deformations

7) C J Ballhausen *Trans Faraday Soc* **57** 1111 (1962

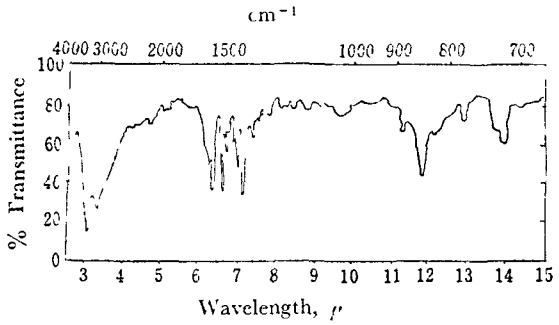

Fig. 1(a). $TiCl_4$ complex

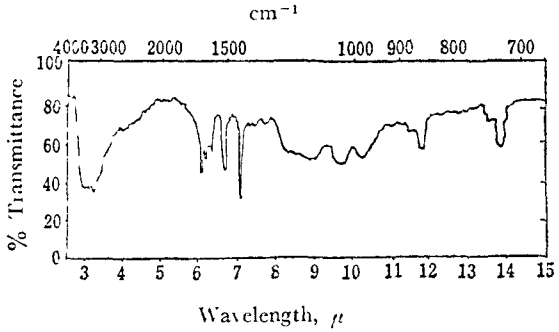

Fig. 1(b). $VOSO_4$ complex

Clark[1] has assigned the 868, 848, 734, and 718 cm^{-1} frequencies in $TiCl_4$(phen) and the 782, 845, 737, and 720 cm^{-1} frequencies in $VOCl_2$-(phen) to out-of-plane hydrogen-deformation vibrations. He has given the region from 300 to 380 cm^{-1} to M–Cl vibrations, which we did not study. Schilt and Taylor[8] have mentioned the possibility that the bands in the orthophenanthroline complexes in the 1125—1250 cm^{-1} region may be due to in-plane hydrogen-deformation motions or to ring vibrations. The vanadium oxygen stretching frequency is located at 890 cm^{-1}[1] in $VOCl_2$(phen) and at 995 cm^{-1} in vanadyl acetylacetone[9]; therefore, we may presume it to be located at 1040 cm^{-1}, since at 980 cm^{-1} a feeble peak is observed in the case of phenanthroline also. The peaks in phenanthroline at 1423, 1505, and 1590 cm^{-1} are shifted to higher frequencies on coordination (in the titanous complex 1450, 1550, and 1600 cm^{-1}; in the vanadyl complex, 1430, 1512, and 1660 cm^{-1}), as has been observed by Schilt and Taylor[8] in a large number of complexes of orthophenanthroline. It was also observed that there is quite a strong absorption peak at 3350 cm^{-1} in orthophenanthroline, a peak which is shifted to 3120 cm^{-1} in the vanadyl complex, whereas in the titanous complex the peak at this frequency becomes very strong and another peak appears at 3100 cm^{-1}. In view of the present data, it is not plausible to assign any frequency to the metal-nitrogen coordinate bond in orthophenanthroline.

The authors are thankful to Professor A. R. Kidwai for providing them with facilities with which to carry out these investigations.

8) A. A. Schilt and R. C. Taylor, *J. Inorg. Nucl. Chem.*, **9**, 211, (1959).
9) C. G. Barraclough, J. Lewis and R. S. Nyholm, *J. Chem. Soc.*, **1959**, 3552.

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10

Spectrophotometric Studies on the Complexes of 3-Nitroalizarin with Lanthanum, Cerium, Praseodymium, Neodymium and Samarium

Jamil Ahmad, Naseer Ahmad and S. M. F. Rahman

Bradford, Geyer and Smith[1] mentioned the formation of cobalt, nickel and copper complexes and described their absorption spectra in the visible range. Recently Kiel and Heertjes[2] prepared Ca-Al, Ca-Fe, Ca-Cr and Ca complexes of 3-nitroalizarin and established their structure by analysis and infra red spectra.

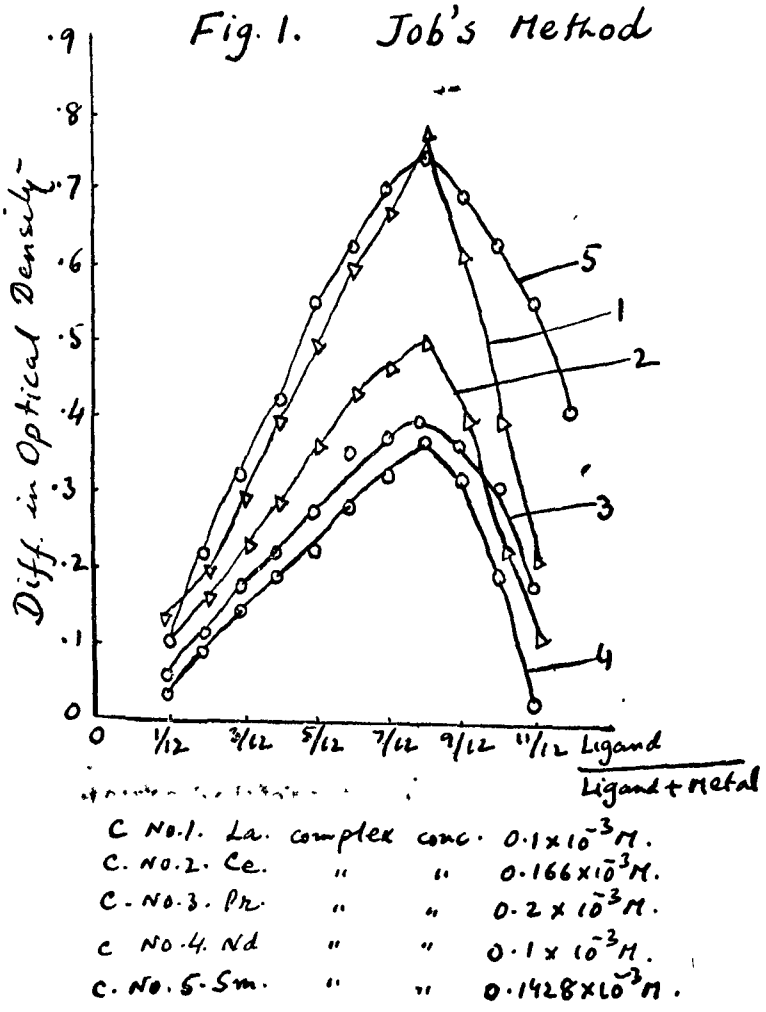
La, Ce, Pr, Nd and Sm form pink coloured complexes with 3-nitroalizarin, which are not mentioned in the existing chemical literature. The results of the spectrophotometric studies on these complexes are being presented in this communication.

Procedure : Nitroalizarin (0.07125 gm. I.C.I., England) was dissolved in 95% ethanol (250 ml.) to obtain 0.1×10^{-2}M solution. $LaCl_3$, $CeCl_3$, $PrCl_3$, $NdCl_3$ and $SmCl_3$ (A.R. samples chemistry Division, AEE., Bombay) were used to prepare their stock solutions in 95% ethanol. A known volume of the stock solution was evaporated to dryness, dissolved in distilled water and the rare-earth precipitated as oxalate[3] and titrated with permanganate. Bausch and Lomb spectromic-20 colorimeter was employed for optical density measurements. Wave length of maximum absorbance was selected with Vosburgh and Cooper method[4]. 0.1×10^{-2} M solutions of the dye and the rare earths were mixed in the molar ratios of 1 : 0, 1 : 1, 1 : 2, 1 : 3, 2 : 1 and 3 : 1 and their optical densities were measured in the visible range. The λmax. was between 520 and 550 mμ for La, Ce, Pr, Nd, Sm complexes and 430 mμ for the pure dye respectively.

1. Bradford P. Geyer and George Mc P. Smith., *J. Amer Chem. Soc.*, 1942, **64,** 1649.
2. E. G. Kiel and P. M. Heertjes, *J. Soc. Dyers Colourists*, 1963, **79,** 186, 1963, **79,** 363.
3. James Frederick Spencer, "The Metals of the Rare-earths", Longmans Green and Co., London (1919), 105.
4. W. C. Vosburgh and G. R. Cooper, *J. Amer. Chem. Soc.*, 1950, **72,** 4488

The validity of Lambert and Beer's law was found in the concentration range of $.5\times10^{-5}$— 0.8×10^{-4} M for these complexes.

Job's method of continued variations[5] was performed at the corresponding wavelength maxima with 0.166×10^{-5}M, 0.125×10^{-5}M and 0.1×10^{-5}M solutions of the dye and the rare-earth salts The difference in the optical densities of the mixutres of the dye and a rare-earth salt and of the corresponding concentration of the dye, was plotted against the composition of the mixture. The rare-earth salt solutions are colourless at such dilutions and possess no appreciable absorption. (Fig. 1).

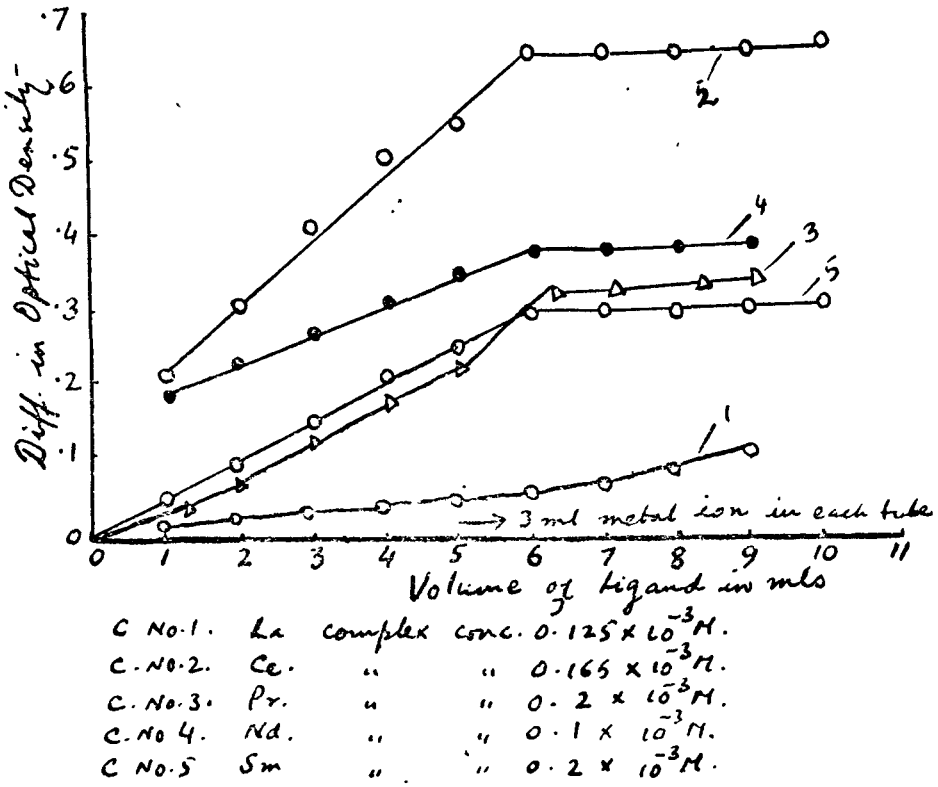


Molar ratio method[6] was employed to confirm the results of Job's method. 3 ml. portions of a rare-earth salt were taken in 12 test tubes and varying volumes of nitroalizarin of the same concentration were added making the total volume 15 ml. by adding re-

5. P. Job, *Compt. rend.*, 1925, **180**, 928.
6. J. H. Yoe and A. L. Jones, *Ind. Eng. Chem. Anal. Ed.* 1944, **16**, 111,

quisite amount of 95% ethanol. Corresponding concentrations of the dye were also prepared in 12 test tubes and the optical densities of both the sets measured. The difference in optical density was plotted against the volume of the dye. (Fig. 2).

Fig. 2. Molar Ratio Method

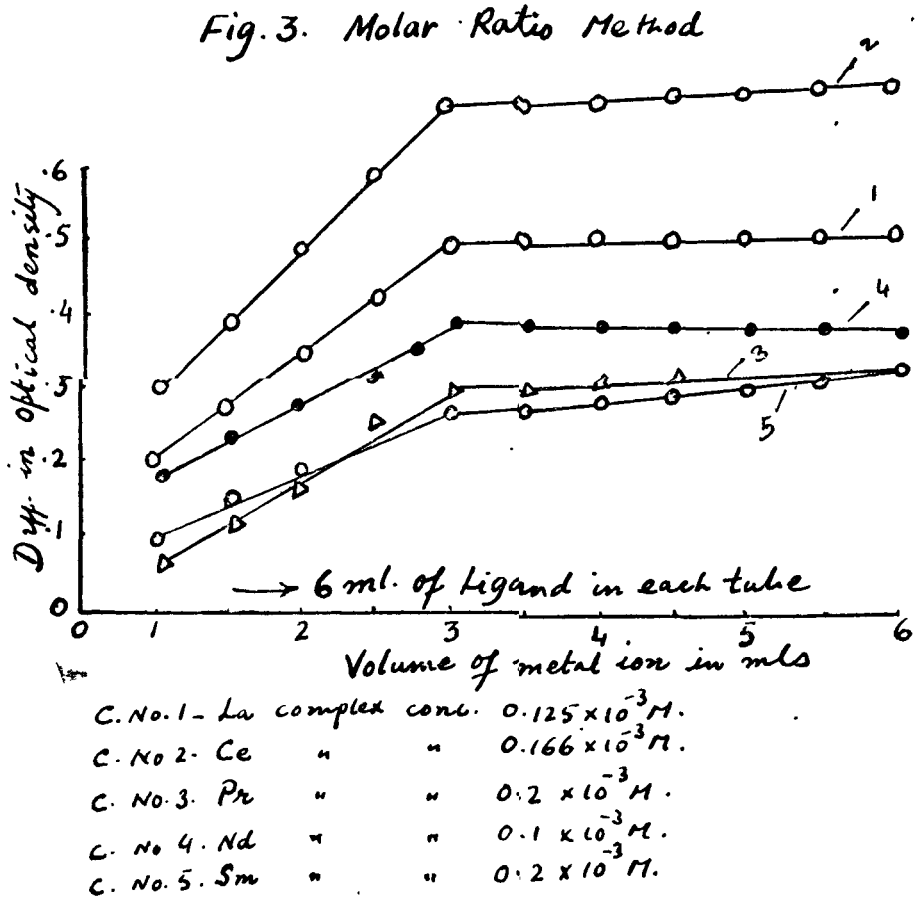


In another set of experiments, 6 ml. portions of the dye were taken in 12 test tubes to which varying volumes of the rare-earth salt solution added. The difference in the optical densities of these mixtures and the optical density of the constant concentration of the dye was plotted against the volume of the rare-earth salt solution (Fig. 3).

For determining the formation constant, the Job's curves were drawn with the optical density of the mixture as Y axis and the constants calculated according to the method of Banerji and Dey[7].

Job's method yielded the molar ratio of 1 : 2 (metal: ligand) for the complexes of lanthanum, cerium, praseodymium, neodymium and samarium with 3-nitroalizarin. The

7. S. K. Banerji and A. K. Dey, *J. Ind. Chem. Soc.*, 1961, **38**, 121.



log of formation constant and the free energy of formation were calculated to be of the order of 11.0±0.3 and—15.0±0.4 Kcals./mole respectively for these complexes.

Thanks are due to Prof. A.R. Kidwai, for providing facilities in the department and to I.C.I., England for providing the samples of the dye as a gift.

Department of Chemistry,
Aligarh Muslim University,
Aligarh.

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Spectrophotometric Studies on the Complexes of 1:2:4-trihydroxyanthraquinone with Some Rare-Earth Salts

Jamil Ahmad, Naseer Ahmad and S. M. F. Rahman

Lanthanum, cerium, praseodymium, neodymium and samarium chlorides interact with 1:2:4—trihydroxyanthraquinone forming pink coloured complexes which have been studied spectrophotometrically. The wavelength of maximum absorption for the dye and the complexes were 480 and 520 mμ respectively. The concentration ranges, in which Lambert and Beer's law is applicable have been ascertained. The ratio in which the rare earth salt and the dye react to form the complexes, has been found to be 1:2 by Job's method and molar ratio method. The log of apparent stability constant for these complexes is 9.1 ± 0.2.

Flumiani and Bajic[1] in their studies on the reactions of hydroxyanthraquinones, observed that 1 : 2 : 4-trihydroxyanthraquinone (purpurin) forms a dark violet normal salt with copper sulphate having the composition $(C_{14}H_5O_2(OH)_2O)_2Cu$. Korenman *et al*[2] reported that purpurin can be used in the detection of scandium at *p*H 2-3 in the presence of yttrium, lanthanum, cerium and aluminium. Korenman and Kornakova[3] investigated the complex formation of Zr^{+4} with purpurin. Yampol Skii[4] mentioned the use of purpurin in the analysis of gallium and indium.

Chlorides of lanthanum, cerium, praseodymium, neodymium and samarium form pink coloured complexes with purpurin which find no mention in the existing literature. Spectrophotometric studies on these complexes are being presented in this communication.

PROCEDURE AND RESULTS

0.6405 gm. of 1 : 2 : 4-trihydroxyanthraquinone was dissolved in 95% ethanol in a 250 ml flask to obtain 0.01M solution. For preparing the standard solutions of the rare-earth salts, $LaCl_3$, $CeCl_3$, $PrCl_3$, $NdCl_3$ and $SmCl_3$ (A.R. samples, Chemistry Division, A.E.E., Bombay) were dissolved in double distilled water. The solutions were standardized[5] by precipitating the rare-earth as oxalate, treating with dilute sulphuric acid and titrating the resulting oxalic acid with standard permanganate solution. Bausch and Lomb spectronic 20 colorimeter was employed for spectrophotometric measurements.

1. G. Flumiani and V. Bajic, *Monatsh*, 1942, **74**, 92-9; Sitzber, Akad. Wiss. Wien, Math-naturw. Klasse Abt. 1942, 2b, **151**, 26-34; *Chem. Abs.*, 1944, **38**, 354.

2. I. M. Korenman, V. P. Guina and L. K. Trifonova, *Zhur. Anal. Khim.*, 1959, **14**, 547-9; *Chem Abs.*, 1960, **54**, 9608e.

3. I. M. Korenman and A. A. Kornakova, *Trudy Khim. i Khim., Tekhnol*, 1959, **2**, 548-54; *Chem. Abs.*, 1962, **56**, 288e.

4. M. Z. Yampol' Skii, Trudy Komissii, *Anal. Khim. Akad. Nauk*, S.S.S.R., Inst. Geokhim. i Anal. Khim, 1960, **11**, 5-12; *Chem Abs.*, 1961, **55**, 11177h.

5. J. F. Spencer, "The Metals of the Rare-earths", Longmans, Green & Co., London, 1919, pp. 105-6.

Vosburgh and Cooper method[6] was used for wave length selection Mixtures of purpurin and rare earth salts were taken in the molar ratios of 1 1, 1 2, 1 3, 2 1 and 3 1 and pure purpurin solution, in ethanolic media and their optical densities measured in the visible range The wavelength of maximum absorption was 520 mμ for the complexes with La, Ce, Pr, Nd and Sm and 480 mμ for the dye

Lambert and Beer's law was found to hold good for 1 2, 1 3 and 1 4 mixtures (metal dye) in the concentration ranges of $0\ 33\times10^{-5}$—$4\ 0\times10^{-5}$ M, $0\ 25\times10^{-5}$–$3\ 0\times10^{-5}$ M and $0\ 2\times10^{-5}$—$2\ 5\times10^{-5}$ M, for La, Ce, Pr, Nd and Sm complexes

Job's method[7], performed at the wavelength of maximum absorption and using $0\ 1\times10^{-3}$M and $0\ 125\times10^{-4}$M solutions of the reactants, yielded the molar ratio of 1 2 (metal dye)

Molar ratio method[8] was used to confirm the results of Job's method 3 ml portions of a rare earth salt of the concentration of $0\ 1\times10^{-3}$ or $0\ 125\times10^{-4}$M were taken in nine test-tubes to which varying volumes of an equimolar solution of the dye added, the total volume made 12 ml by adding requisite amount of ethanol and the optical densities of the mixtures determined Similar concentrations of the dye were taken in nine test-tubes making the total volume 12 ml with ethanol and the optical densities measured The difference in optical density was plotted against the volume of the dye and the ratio was found to be 1 2 (metal dye) The same ratio emerged when a constant volume of the dye was used and varying volumes of the rare-earth salt solution mixed

The log of apparent stability constant was calculated by the method of Dey and Banerji[9] using Job's curves with optical density as the ordinate and the composition of the mixtures as abscissa and the value was found to be $9\ 1\pm0\ 2$.

The authors are thankful to Prof A R Kidwai for providing facilities to carry out these investigations

Department of Chemistry,
Aligarh Muslim University,
Aligarh

Received, November 25, 1966

6 W C Vosburgh and G R Cooper, *J Amer Chem Soc*, 1941, **63,** 437
7 P Job, *C R Acad Sci*, Paris, 1925, **180,** 928.
8 A E Harvey Jr and D L Manning, *J Amer Chem Soc*, 1950, **72,** 4488
9. A K Dey and S K Banerji, *this Journal*, 1961, **38,** 139-46.

J inorg nucl. Chem., 1967, Vol. 29, pp 2961 to 2964. Pergamon Press Ltd. Printed in Northern Ireland

12

SPECTROPHOTOMETRIC STUDIES ON THE TITANIUM(III) CHROMOTROPIC ACID COMPLEX

M. M. KHAN and N. AHMAD
Department of Chemistry, Aligarh Muslim University, Aligarh India

(*Received* 23 *December* 1966)

Abstract—The titanium(III)-chromotropic acid interaction was studied spectrophotometrically. The red complex showed maximum absorption at 440 mμ in aqueous medium at pH 7 and followed Lambert and Beer's Law in the concentration range of 0·666 × 10^{-3}–0·333 × 10^{-4} M. Job's method, molar and slope ratio methods in aqueous solution at pH 7 exhibit a ratio of 1:1 (Ti^{3+}:ligand). The formation of the complex is very much affected by the pH of the solutions. Job's method at pH 1, 2·2, 4·4 and 5·5, yielded the ratios of 1:2, 1·1, 1·2 and 1:3 (Ti^{3+}:ligand). The log of formation constant and free energy of formation of the complex in aqueous medium at pH 7 were found to be 3·0 ± 0·3 and −4·0 ± 0·4 kcal/mole respectively at 25°C.

THE COLOUR reaction between titanium(III) chloride and chromotropic acid (abbreviated in this paper as CTA) does not find mention in the existing chemical literature. This interaction was studied spectrophotometrically and is being presented in this communication.

EXPERIMENTAL

Materials and methods

Titanium(III) chloride[1] was dissolved in air free double distilled water and the strength of the solution was determined by titrating against potassium permanganate.[2] Since titanium(III) chloride is apt to hydrolyse and undergo atmospheric oxidation, fresh solutions were always prepared immediately before use and kept covered with a layer of kerosine oil. E. Merck grade chromotropic acid sodium salt was used to prepare its solution. The colourless aqueous solution of chromotropic acid turns yellow on long exposures to light. Hence fresh solutions were always used and kept in amber coloured bottles.

Absorption maxima of the complex was determined by the VOSBURGH and COOPER method[3] Optical densities of solutions of titanium(III) chloride and complexing agent and their mixtures in the ratio of 1·1, 1·2, 1·3, 2·1 and 3·1 were measured with Bausch and Lomb Spectronic-20 Colorimeter at wavelengths in the visible range. The optical density, is highest at 350 mμ. It decreases rapidly with increase in wavelength, comes to a minimum at about 390 mμ and remains almost steady up to 600 mμ except for a meagre rise at 440 mμ (Fig. 1).

Lambert and Beer's law was found to hold good in the concentration range of 0·666 × 10^{-3}–0·333 × 10^{-4} M.

RESULTS AND DISCUSSION

Job's method.[4] Solutions of titanium(III) chloride and the complexing agent were mixed in different ratios and their optical densities determined at the corresponding maxima. The optical densities for the same concentrations of the complexing

[1] J. W. MELLOR, *Inorganic and Theoretical Chemistry*, Vol. 7, p. 74. Longmans Green, London (1927)
[2] CUMMING and KAY, *Quantitative Chemical Analysis* p. 150 Oliver & Boyd, London (1956)
[3] W. C. VOSBURGH and G. R. COOPER, *J. Am. chem. Soc.* **63**, 437 (1941).
[4] P. JOB, *C.r. Rebd. Acad. Sci. Séanc. Paris* **180**, 928 (1925).

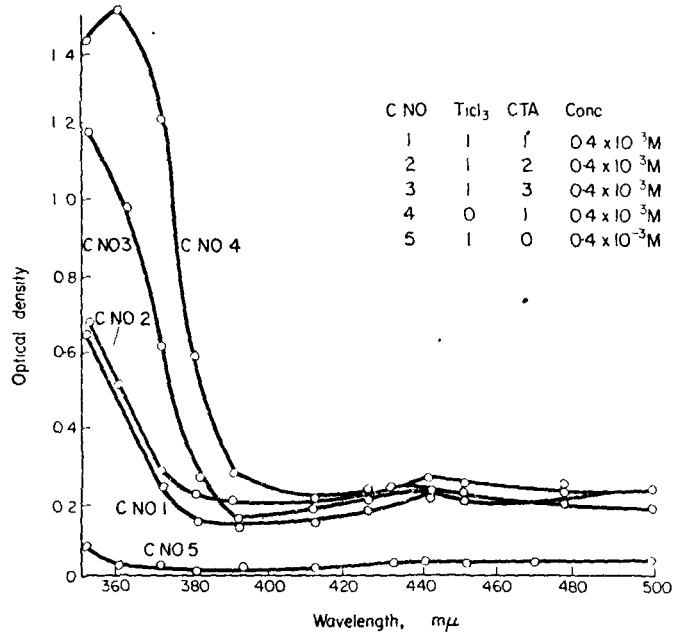

FIG. 1.—VOSBURGH and COOPER method.[3]

TABLE 1.—λ_{max} FOR 1:1, 1:2 AND 1:3 METAL:DYE MIXTURES AT VARIOUS pH VALUES

pH values	1·0	2–2·8	3·7	5·0–5·57
λ_{max}(mμ)	460	470	450	430

agent were also determined and the difference plotted against the composition of the mixture. The ratio of 1:2 (Ti^{3+}:CTA) in hydrochloric and sulphuric acids of pH 1 was observed. At pH 2·2, 4·4 and 5·5 the ratios of 1:1, 1:2 and 1:3 emerged (Fig. 2). When the pH of mixtures was brought to 7 the ratio of 1:1 was observed.

Molar ratio method.[5] Titanium(III) chloride solution (4 ml of $0{\cdot}1 \times 10^{-2}$ M) was taken in twelve test tubes to which varying volumes of chromotropic acid of the same concentration were added separately and the total volume made 12 ml by adding requisite amount of water. In another set of twelve test tubes the same volumes of the same chromotropic acid solution taken and the final volume made 12 ml with water. The optical densities were determined and the difference plotted against the volume of chromotropic acid. The pH of the various mixtures was brought to 7 invariably.

In another set, to the constant volume of chromotropic acid varying volumes of titanium(III) chloride were added. The optical densities of these mixtures and chromotropic acid (4 ml CTA + 8 ml water) were determined and the difference plotted against the volume of titanium(III) chloride. The ratio of 1:1 was observed in both the cases (Fig. 3).

Slope ratio method. Titanium(III) chloride solution (8 ml, $0{\cdot}5 \times 10^{-3}$ M concentration) was taken in twelve test tubes separately and the varying volumes of the

[5] A. E. HARVEY Jr. and D. L. MANNING, *J. Am. chem. Soc.* **72**, 4488 (1950).

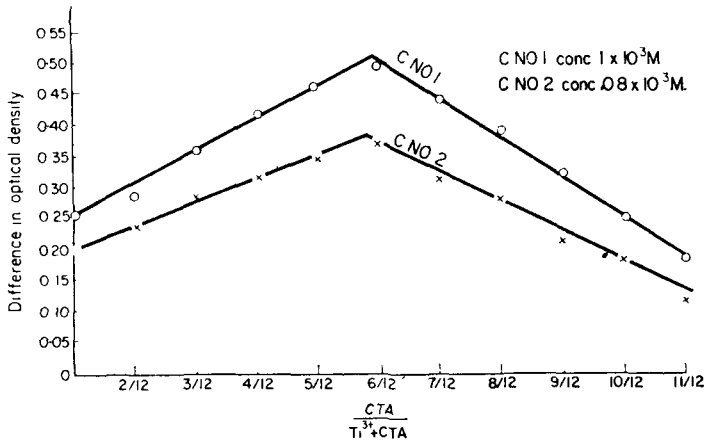

FIG. 2.—JOB's method at pH 7[4].

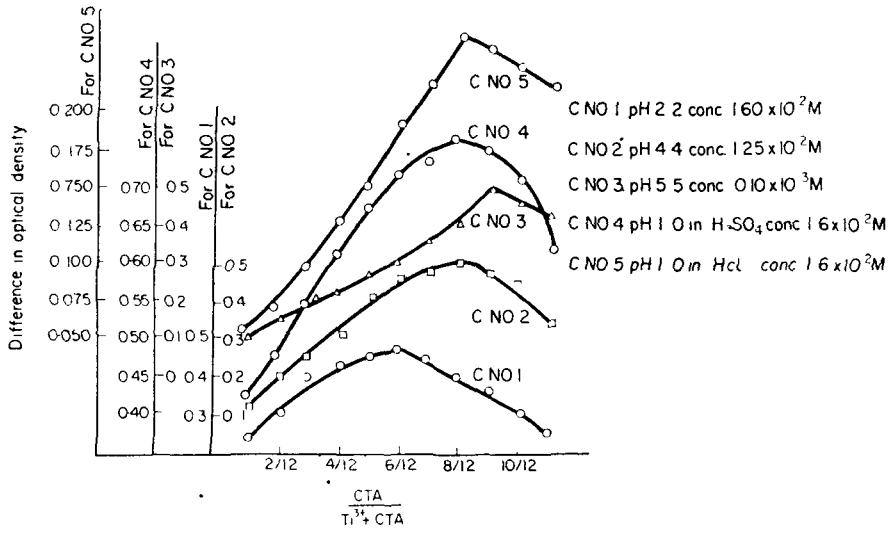

FIG. 3.—Jobs' method at different pH[4].

complexing agent added making the total volume constant, i.e. 12 ml by adding water. Similarly in twelve test tubes 8 ml of chromotropic acid was taken and varying volumes of titanium(III) chloride added keeping the total volume constant as above. The pH of the solutions was maintained at 7. The optical densities were measured and plotted against the volume of the variable reagent. The ratio of the slopes of the two lines (1:1) is the ratio between the two reactants (Fig. 4).

The value of formation constant was calculated from Job's curves (Fig. 5). The equation used was

$$X = \frac{x}{(a_1 - x)(b_1 - x)} = \frac{x}{(a_2 - x)(b_2 - x)}$$

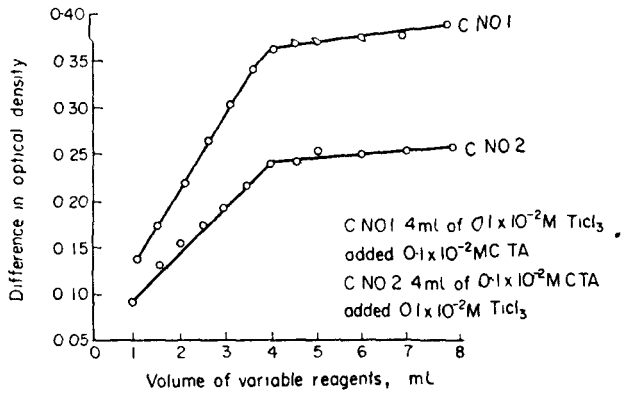

FIG. 4.—Molar ratio method.

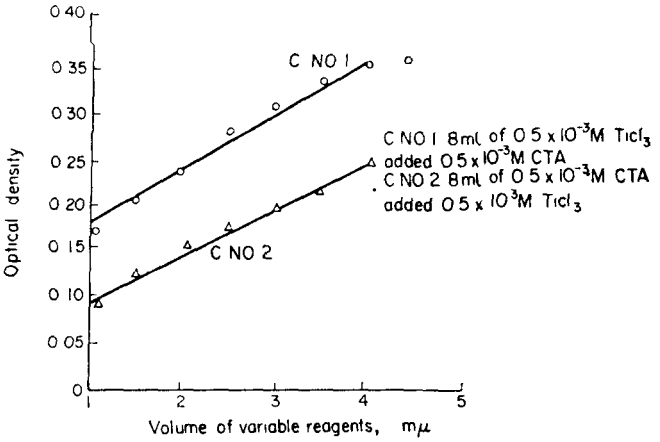

FIG. 5.—Slope ratio method.[4]

where a_1, a_2 and b_1 and b_2 are the molar concentrations of titanium(III) chloride and chromotropic acid at two points on two curves of Job's method, such that the optical density on these two points was the same. Consequently it could safely be assumed that the quantities of the complex formed at them were equal thus making the value of x the same in both the cases. The values of log K and free energy of formation ($\Delta F = -RT \ln K$) were calculated to be $3{\cdot}0 \pm 0{\cdot}3$ and $-4{\cdot}0 \pm 0{\cdot}4$ kcal/mole respectively at 25°C.

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Nitroprusside Complexes of Divalent Cobalt, Nickel, Cadmium, Zinc, Copper, Manganese, Iron, and Trivalent Titanium

By Mohd. Mahfooz Khan and Naseer Ahmad

With 3 Figures

Summary

The formation of slightly soluble $M^{II}[Fe(CN)_5NO](\cdot 2\,H_2O)$ complexes of transition metals and of $Ti^{III}[Fe(CN)_5NO]Cl$ is investigated by means of analyses, electrometric and thermometric titrations.

Inhaltsübersicht

Es wird die Bildung schwerloslicher $M^{II}[Fe(CN)_5NO](\cdot 2\,H_2O)$-Komplexe von Übergangsmetallen sowie des $Ti^{III}[Fe(CN)_5NO]Cl$ analytisch und durch elektrometrische und thermometrische Titration untersucht.

Sodium nitroprusside has long been used in the detection of sulphur in organic compounds. The alkali metal sulphides react with sodium nitroprusside forming a complex having the composition $[Fe(CN)_5NOS]$[1]. Scagliarini[2] isolated the reaction product of nitroprusside and sulphide in methyl alcohol as violet crystals and gave the composition as $Na_4[Fe(CN)_5NOS]$. He further observed that the Bodekar reaction between sodium nitroprusside and sulphite ion depends upon the formation of the coloured ion $[O\cdot N(SO_3)---Fe^{++}---(CN)_5]^{IV}$ which forms a salt with cadmium. He later on reported that the ion forms salts of the type $M_2[Fe(CN)_5NOSO_3]\cdot 12\,H_2O$ $2\,C_6H_{12}M_4$ in the presence of hexamethylene tetramine with some metal salts [M = Cd, Zn and Ni$(8\,H_2O)$]. Gusev and Belles[3] reported the reaction of ferric sulphate and antipyrine with sodium nitroprusside and found that $[Fe(C_{11}H_{12}ON_2)_3]_2[Fe(CN)_5NO]_3$ is produced. In 1950 Brustier and

[1]) G. Scagliarini and P. Pratesi, Atti Accad. Lincei **13**, 199 (1931), Chem. Abstr. **25**, 5636 (1931).

[2]) G. Scagliarini, Atti IV Congr. Chim. pura applicata **597**, 1933 (1932); Chem. Abstr. **29**, 2873[1] (1935); G. Scagliarini, Atti Accad. Lincei **22**, 155 (1935), Chem. Abstr. **30**, 6670[4] (1936); G. Scagliarini and F. Monforte, Atti Accad. Lincei **20**, 41 (1934), Chem. Abstr. **29**, 3622[9] (1935).

[3]) S. I. Gusev and R. G. Belles, Ž. obšč. Chim. (J. allg. Chem. [UdSSR]) **21**, 1971 (1951); Chem. Abstr. **46**, 3442[c] (1952).

FERNANDEZ[4]) isolated a blue solid $[Na_6(Fe_2(CN)_8S_2)]_n$ from the products of the Lyon Playfair reaction (sodium nitroprusside — sodium sulphide) ROSI[5]) used the interaction of sodium nitroprusside with tetracyano nickelate in the presence of an alkali for the quantitative estimation of nitroprusside

$$4\,Na_2[Fe(CN)_5NO] + 10\,NaOH + Na_2Ni(CN)_4$$
$$= 4\,Na_4Fe(CN)_6 + 4\,NaNO_2 + 4\,H_2O + Ni(OH)_2$$

By determining the amount of nickel with dimethyl glyoxime in the liberated $Ni(OH)_2$ it was possible to calculate the amount of nitroprusside

Sodium nitroprusside reacts in aqueous solution with some metal ions viz., Co^{++}, Ni^{++}, Cd^{++}, Zn^{++}, Cu^{++}, Mn^{++}, Fe^{++} and Ti^{+++} giving differently coloured precipitates but strangely enough do not find mention in the existing chemical literature. The formation of these complexes has been studied in aqueous solution using direct and reverse conductometric and thermometric titrations. The complexes were isolated and analysed and the results are being presented in this communication.

Experimental

Standard solutions of the chlorides of cobalt[6]), nickel[7]), cadmium[8]), zinc[9]), copper[10]) and manganese[11]) and iron sulphate[12]) were prepared from B D H Analar or E Merck products. Standard solution[13]) of titanium(III) chloride was prepared from $TiCl_3 \cdot 6H_2O$ crystals[14]). The standard solution of sodium nitroprusside was prepared by dissolving the requisite amount of $Na_2Fe(CN)_5NO \cdot 2H_2O$ (B D H A.R.) in air free conductivity water. Since titanium(III) chloride is apt to hydrolyse and undergo atmospheric oxidation fresh solutions were always prepared before use and kept covered with a layer of kerosene oil throughout these investigations.

Direct and reverse conductometric titrations were performed using solutions of metal salts and nitroprusside in conductivity water. In the case of titanium(III) chloride air free conductivity water was used. For measuring conductivity Philips conductivity bridge PR model 9500 was used (Fig. 1).

For thermometric titrations, a well insulated DEWARS flask of 100 ml capacity was used. The burette was wrapped with asbestos on all sides except for the streak left to make the graduations visible. The solutions were kept for sometime to attain room temperature

[4]) V. BRUSTIER and H. GARCIA FERNANDEZ, Bull. Soc. chim. France **1950** 1262, Chem. Abstr. **45**, 6114d (1951).

[5]) P. H. ROSI, Z. analyt. Chem. **143** 195 (1954), Chem. Abstr. **49** 99b (1955).

[6]) A. C. CUMMING and S. A. KAY, Quantitative Chemical Analysis, XI Edn. p. 353, London 1956.

[7]) Ibid. p. 371.

[8]) Ibid. p. 328 and 327.

[9]) Ibid. p. 407.

[10]) Ibid. p. 159.

[11]) Ibid. p. 127.

[12]) Ibid. p. 291.

[13]) I. VOGEL, Quantitative Inorganic Analysis, II Edn. p. 318, London 1959.

[14]) J. W. MELLOR, Inorganic and Theoretical Chemistry, Vol. 7, p. 74, London 1927.

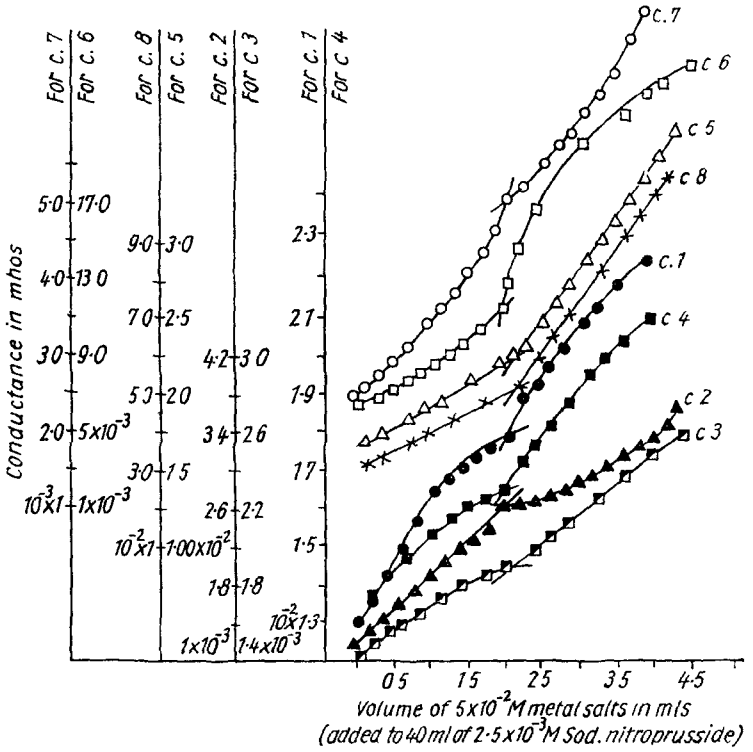

Fig. 1. Conductometric titrations.
C. 1 with $CoCl_2$
C. 2 with $NiCl_2$
C. 3 with $CdCl_2$
C. 4 with $ZnCl_2$
C. 5 with $CuCl_2$
C. 6 with $MnCl_2$
C. 7 with $FeSO_4$
C. 8 with $TiCl_3$

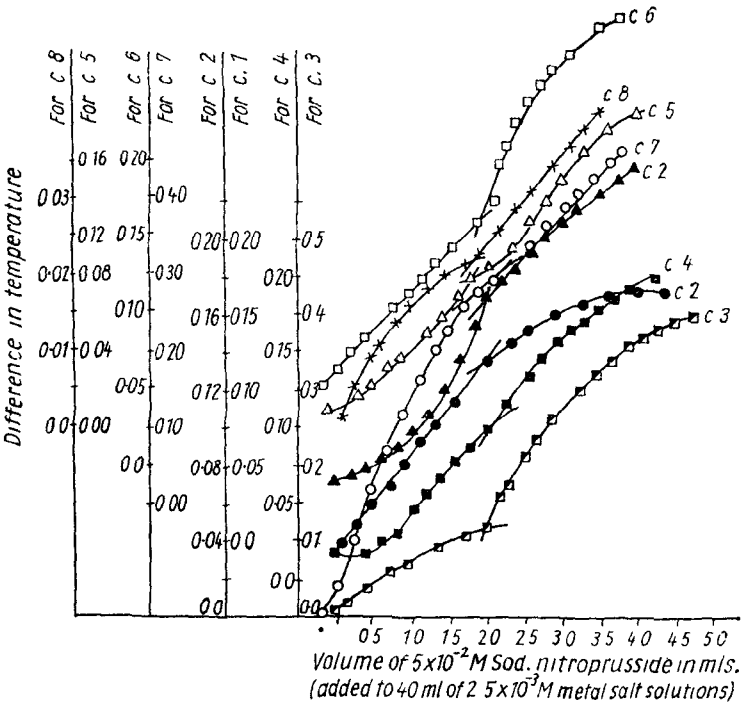

Fig. 2. Thermometric titrations.
C. 1 with $CoCl_2$
C. 2 with $NiCl_2$
C. 3 with $CdCl_2$
C. 4 with $ZnCl_2$
C. 5 with $CuCl_2$
C. 6 with $MnCl_2$
C. 7 with $FeSO_4$
C. 8 with $TiCl_3$

before actually starting the titrations. Variations in temperature were noted by a BECKMANN thermometer. Both direct and reverse titrations were carried out (Fig. 2).

The potentiometric titrations were performed with the help of a Tinsley potentiometer using a lamp and scale outfit. Only direct titrations in the cases of cobalt, copper and titanium could yield any results (Fig. 3).

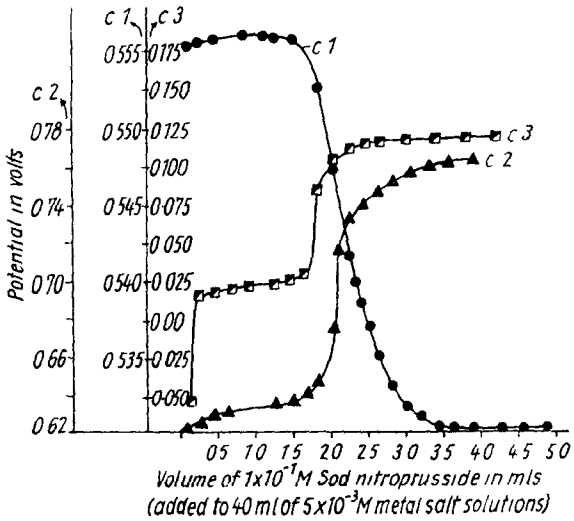

Fig. 3. Potentiometric titration
C 1 with $CoCl_2$
C 2 with $CuCl_2$
C 3 with $TiCl_3$

The complexes were prepared by mixing aqueous solutions of metal salts and sodium nitroprusside in equimolecular proportions. The precipitate was centrifuged, washed first with water and then repeatedly with 50% ethanol till the centrifugate was free from metal salt and nitroprusside. The precipitates of manganese and titanium complexes were obtained in methyl alcohol. The precipitates were dried in a vacuum desiccator over quick lime for several days. The colours of the dried complexes of cobalt, nickel, cadmium, zinc, copper, manganese, iron and titanium were dirty pink, almost black, light buff, light rose coloured, bluish green, almond coloured, baked clay coloured and black respectively.

A weighed quantity of the cobalt complex was fused with fusion mixture in a platinum crucible and dissolved in dilute nitric acid. Iron was separated as hydroxide, dried, ignited and weighed as Fe_2O_3[12]), the filtrate evaporated to dryness, dissolved in dilute hydrochloric acid, cobalt precipitated with α nitroso β naphthol and weighed as cobalt sulphate[6]).

The fused nickel complex was dissolved in dilute hydrochloric acid and then nickel and iron were separated and estimated according to the method used for nickel steel[15]).

The cadmium complex was fused, dissolved in dilute sulphuric acid and cadmium estimated[8]) as sulphate after first precipitating it as sulphide and then iron was determined as hydroxide.

From the solution of the fused zinc complex in dilute hydrochloric acid, iron was precipitated as hydroxide[16]) in the presence of excess of ammonium chloride and then zinc precipitated and weighed as zinc ammonium phosphate[9]).

[15]) CUMMING and KAY's book, XI Edn. 1956, loc. cit., p. 127 and 371.
[16]) CUMMING and KAY's book, IX Edn. 1944, p. 319.

Table 1
Analyses of the complexes

Cobalt Complex	Co	Fe	N	C	H_2O
Calculated for $Co[Fe(CN)_5NO] \cdot 2H_2O$	18.96%	17.96%	27.02%	19.36%	11.58%
Observed	19.1 %	18.1 %	26.40%	18.5 %	12.68%

Nickel Complex	Ni	Fe	N	C	H_2O
Calculated for $Ni[Fe(CN)_5NO] \cdot 2H_2O$	18.90%	17.98%	27.04%	19.32%	11.56%
Observed	17.9 %	18.93%	27.02%	18.4 %	12.5 %

Cadmium Complex	Cd	Fe	N	C	
Calculated for $Cd[Fe(CN)_5NO]$	34.24%	17.01%	25.59%	18.33%	
Observed	34.8 %	16.8 %	24.44%	17.6 %	

Zinc Complex	Zn	Fe	N	C	H_2O
Calculated for $Zn[Fe(CN)_5NO) \cdot 2H_2O]$	20.60%	17.60%	26.48%	18.91%	11.36%
Observed	20.9 %	19.2 %	25.34%	18.1 %	11.5 %

Copper Complex	Cu	Fe	N	C	
Calculated for $Cu[Fe(CN)_5NO]$	22.74%	19.99%	30.06%	21.44%	
Observed	22.57%	20.5 %	30.1 %	20.8 %	

Manganese Complex	Mn	Fe	N	C	H_2O
Calculated for $Mn[Fe(CN)_5NO] \cdot 2H_2O$	17.89%	18.14%	27.38%	19.56%	11.74%
Observed	17.8 %	17.7 %	25.3 %	18.7 %	13.09%

Iron Complex	Fe	N	C	H_2O
Calculated for $Fe[Fe(CN)_5NO] \cdot 2H_2O$	36.29%	27.33%	19.50%	11.70%
Observed	35.8 %	25.4 %	18.9 %	13.2 %

Titanium Complex	Ti	Fe	N	C	Cl
Calculated for $Ti[Fe(CN)_5NO]Cl$	16.01%	18.66%	28.66%	20.05%	11.80%
Observed	16.6 %	18.0 %	27.6 %	19.6 %	11.3 %

After the necessary fusion and dissolution of the copper complex, copper was estimated as copper(I) thiocyanate[17] and iron as oxide.

From the solution of manganese complex as prepared in other cases, iron was precipitated at pH 4 and manganese at pH 9 as hydroxides[18] and later on manganese estimated as carbonate[19]. The iron complex was fused and total iron estimated as oxide.

The method of decomposition of the titanium complex and subsequent estimation of titanium and iron as oxides was the same as used in the analysis of ferrocarbon titanium[20]. The complex gave test for chloride which was estimated as silver chloride from a separate sample. The sample was dissolved in dilute nitric acid, exdess silver nitrate was added, the precipitate washed with cold water several times in a Gooch crucible, dried and weighed.

For the estimation of water, a weighed quantity of the complex was heated to 80°C in an oven, dried in a vacuum desiccator over fused calcium chloride for several hours and reweighed. The loss in weight gave the amount of water in te complex. Microanalysis was done for the determination of carbon and nitrogen.

Results and Discussion

The results of analysis are given in Table 1.

Direct and reverse conductometric titrations in the case of cobalt, nickel, cadmium, zinc, manganese and iron and only reverse conductometric titrations in the case of Copper and titanium yielded the molar ratio of 1:1 (metal:nitroprusside). This ratio was confirmed in all cases by both direct and reverse thermometric titrations. In the case of cobalt, copper and titanium, direct potentiometric titrations further lent support to the ratio determined earlier.

Chemical analysis showed beyond doubt that the following formulae should be assigned to these complexes.

$Co[Fe(CN)_5NO] \cdot 2\,H_2O$	$Cu[Fe(CN)_5NO]$
$Ni[Fe(CN)_5NO] \cdot 2\,H_2O$	$Mn[Fe(CN)_5NO] \cdot 2\,H_2O$
$Cd[Fe(CN)_5NO]$	$Fe[Fe(CN)_5NO] \cdot 2\,H_2O$
$Zn[Fe(CN)_5NO] \cdot 2\,H_2O$	$Ti[Fe(CN)_5NO] \cdot Cl.$

Authors' thanks are due to Prof. A. R. Kidwai for providing facilities in the department.

[17]) Cumming and Kay's book, XI Edn. 1956 loc. cit., p. 415 and 342.

[18]) Ibid. p. 351.

[19]) Ibid. p. 362.

[20]) W. W. Scott, Standard Methods of Chemical Analysis, Vol. I, V Edn., p. 984, New York 1939.

Aligarh, U. P. (India), Aligarh Muslim University, Department of Chemistry.

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14

Studies on the Complexes of Alizarin, Quinalizarin and Erichrome Blue Black R with some Rare Earth Salts

S. M. F. Rahman, Naseer Ahmad and Jamil Ahmad

Alizarin, Quinalizarin and Eriochrome Blue Black R form red, light blue, and dark brown coloured complexes with La, Ce, Pr, Nd and Sm. These complexes have been studied spectrophotometrically. The λmax. for alizarin complexes was 535-40 mμ and that for quinalizarin and Erichrome Blue Black R were 575-85 and 530-35 mμ respectively. Job's method of continuous variation as well as molar ratio method showed a combining ratio of 1:2 (metal:dye) for alizarin and quinalizarin complexes and 1:1 for Eriochrome-rare-earth complexes. The log of apparent formation constant for the Eriochrome complexes was 5.2 ± 0.8.

A-lieva et al[1] reported colour reaction of quinalizarin with Y^{+3}, La^{+3}, Ce^{+3}, Pr^{+3}, Nd^{+3} and Gd^{+3} in slightly acidic medium. Korenman[2] and others, in their investigations on the interaction of rare-earths with alizarin reds and quinalizarin ascertained that all rare earth complexes exhibit maximum absorption in the wave length range of 560-90 mμ and reported a combining ratio of 1 : 1 for various rare-earth elements and quinalizarin. Tataeve and Bagdasaror[3] used quinalizarin in the photometric determination of praseodymium. They reported no colour development in the *p*H range of 1—6.5; complex formation at higher *p*H values, λmax at 584 and 658 mμ at *p*H 7 and 8 — 10 respectively and a molar ratio of 1 : 2 for complex formed between praseodymium and quinalizarin. Lal and Srivastava[4] have proposed alizarin as a reagent for quantitative analysis of a mixture containing Ce(III) and Ce(IV). The interaction between rare earth salts and Eriochrome Blue Black R abbreviated in this paper as EBBR finds little mention in the existing chemical literature.

Our present communication deals with the spectrophotometric studies on the complexes of La, Ce, Pr, Nd and Sm with alizarin, quinalizarin and EBBR.

EXPERIMENTAL

0.24 gm of alizarin, 0.0544 gm of quinalizarin and 0.416 gm of EBBR were dissolved in 1 litre of 98% alcohol separately to obtain $0.2 \times 10^{-3} M$ solution of quinalizarin and $0.1 \times 10^{-2} M$ solution of the other dyes. The *p*H of alcohol used for alizarin and quinalizarin solutions was adjusted to 6 by adding hydrochloric acid and that for EBBR to 10 by adding requisite amount of caustic soda. $LaCl_3$, $PrCl_3$, $NdCl_3$ and $SmCl_3$ (A. R. samples, Chemistry

1. M. K. Akhmedli, A. A. Sadykhova, P. B. Granovskaya, I. S. Lozovskaya and S. Alieva, *Azerb, Khim. Zh.* (5), 93-104 (1963) (Russ), *Chem. Abs.*, 1965, **62**, 7106c.
2. I. M. Korenman, V. G. Ganina and N. V. Kurina, *Tr po Khim i Khim Tekhnol.*, 1961, **4**, 761-6; *Chem. Abst.*, 1962, **58**, 9602g.
3. O. A. Tataeve and K. N. Bagdasaror, *Elctrokhim i oplich Metody Analiza*, 1963, **8**b, 212-216; *Chem. Abst.* 1964, **61**, 4957a,.
4. Sudarshan Lal and S. N. Srivastava, *J. Chem. Education*, 1966, **43**,(8), 424; *Chem. Abst.*, 1966 **65**, 11314c.

Division, AEE Bombay) were dissolved in 98% alcohol of *p*H 6 or 10 as the case may be to prepare their stock solutions. A known volume of the stock solution was evaporated to dryness, dissolved in distilled water and the rare-earth precipitated as oxalate[5] and titrated with standard permanganate solution.

Bausch and Lomb spectronic-20 colorimeter was used for spectrophotometric measurements.

The wave length of maximum absorptions by the complexes of alizarin, quinalizarin and EBBR was selected according to the method of Vosburgh and Cooper[6]. $0.166\times10^{-3}M$ alizarin, $0.333\times10^{4}M$ or $0\ 2\times10^{-4}M$ solution of quinalizarin or EBBR was mixed with equimolar solution of rare-earth salts in the ratio of 1 :1, 1 : 2, 1 : 3, 2 : 1, 3 : 1 and 1 : 0 and their optical density measured at different wave lengths in the visible range. The λmax. for alizarin and alizarin-rare earths complexes were at 440 and between 535-40 mμ respectively. In the case of quinalizarin and quinalizarin rare-earths complexes they were at 500 and between 575-85 mμ respectively. The same for EBBR and EBBR-rare earths complexes was between 535-40 mμ.

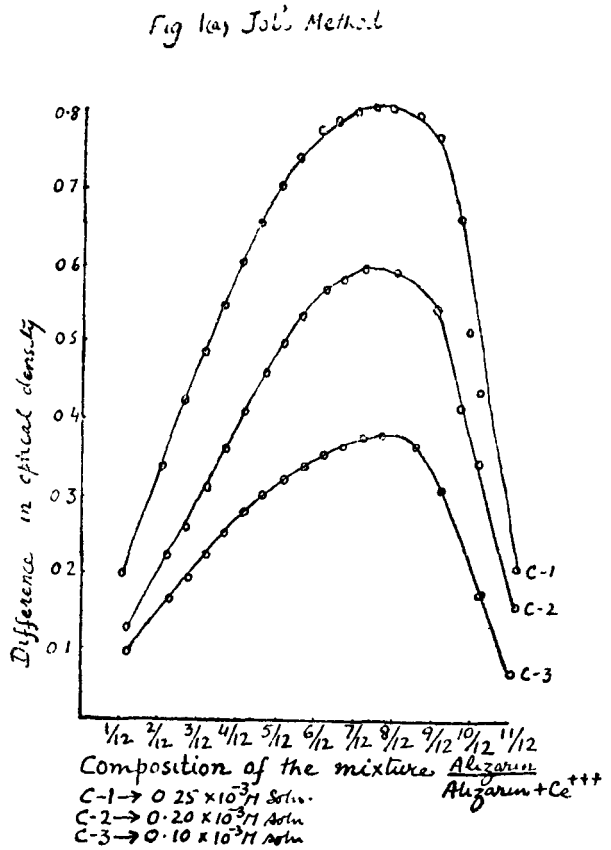

FIG. 1a

5. James Frederick Spencer, "The Metals of the Rare Earths", Longmans Green, London, 1919, pp 110-6
6. W. C. Vosburgh and G. R, Cooper, *J. Amer. Chem. Soc.*, (1941), **63**, 437.

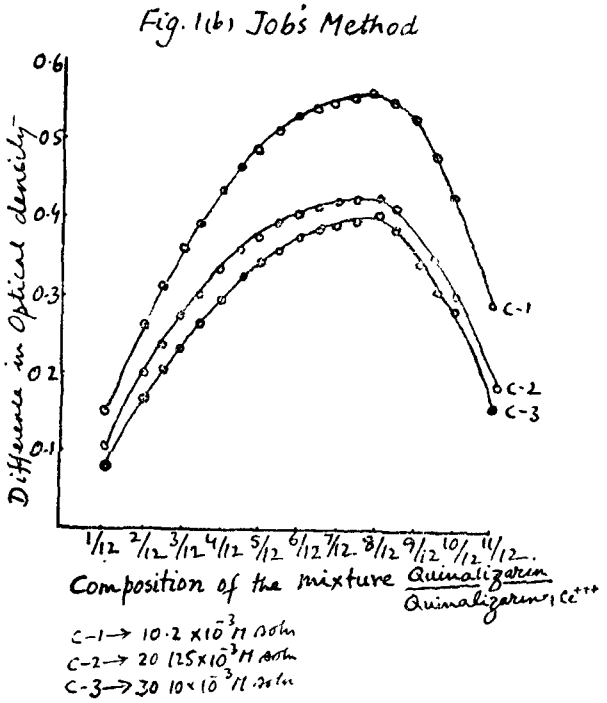

FIG. 1b

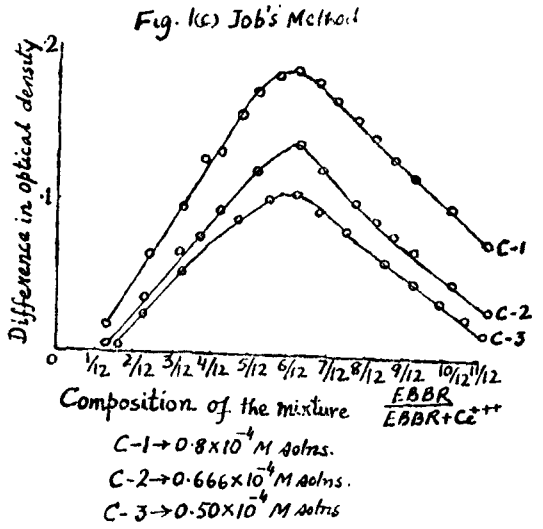

FIG. 1c

Lambert's and Beer's Law was found to hold good in the approximate concentration range of 0.166×10^{-5}—$1.6\times10^{-4}M$, 0.166×10^{-5}—$1.0\times10^{-4}M$ and 0.166×10^{-5}—$0.9\times10^{-4}M$, for the rare-earth alizarin mixtures in the ratio of 1 : 2, 1 : 3 and 1 : 4 respectively. The range for rare earth quinalizarin mixtures in the above ratio was 1.666×10^{-6}—6.66

$\times 10^{-5}M$, 1.666×10^{-5} ——$5.0\times10^{-5}M$ and 1.66×10^{-6} ——$4.0\times10^{-5}M$ respectively. The same for rare-earth EBBR mixtures in the ratio of 1 : 1, 1 : 2 and 1 : 3 was 0.125×10^{-5} ——$6\times10^{-5}M$, 0.125×10^{-5}——$2.7\times10^{-5}M$ and 0.125×10^{-5}——$2.0\times10^{-5}M$ respectively.

Job's method of continuous variation[7] was performed at the corresponding wave length maxima with equimolar concentrations of the rare earth salts and dyes. In the case of alizarin complexes the concentration of the solutions used were $0.25\times10^{-3}M$, $0.20\times10^{-3}M$ and $0.10\times10^{-3}M$. The same for quinalizarin complexes were $0.2\times10^{-3}M$, $0.125\times10^{-3}M$ and $0.10\times10^{-3}M$. Job's method for EBBR rare earths complexes were performed at $0.8\times10^{-4}M$, $0.666\times10^{-4}M$ and $0.50\times10^{-4}M$ concentrations. The difference in the optical densities of the mixture of the dye and the rare-earths salts and the corresponding concentration of the dye was plotted against the composition of the mixture. The rare-earth salts solutions at such a high dilution posssess no appreciable absorption (*fig.* 1a, 1b and 1c).

Molar[8] ratio method was employed to confirm the results obtained from Job's method. 2 ml solution of the rare-earth salt was taken in each of the 12 test tubes and varying volumes of the equimolar concentrations of the dye were added. The total volume was made to 12 ml by adding requisite volume of alcohol. The difference in the optical density was plotted against the volume of the dye.

In another set of experiments the volume of the dye was kept constant at 4 ml and varying volumes of the rare-earth salts solutions were added and the volume was made up

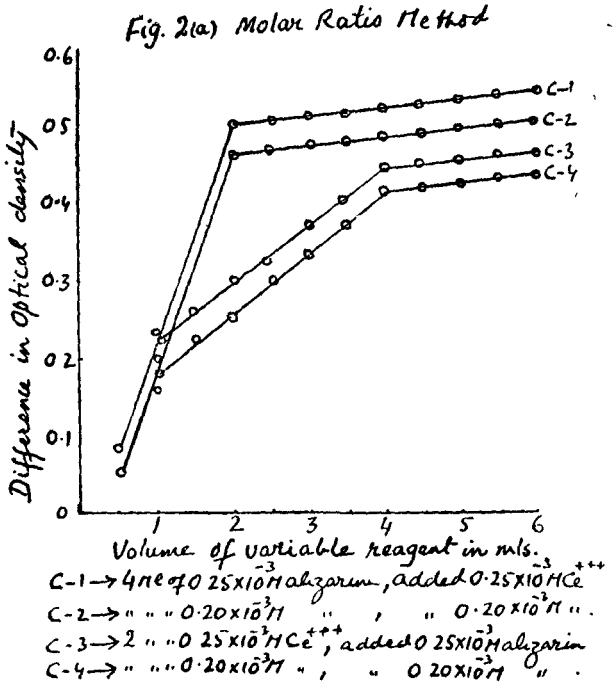

FIG. 2a

7. P. Job, *Compt. rend.*, 1925, **180**, 928.
8. J. H. Yoe and A. L. Jones, *Ind. Eng. Chem. Anal. Ed.* 1944, **16**, 111.

to 12 ml by addition of alcohol. In another test tube 4 ml of the dye was taken and alcohol was added to make the volume 12 ml. The difference in the optical densities of the mixture of the rare-earth-dye and that of the dye were plotted against the volume of the rare-earth. Such experiments were performed for the complexes of alizarin and quinalizarin with La, Ce, Pr, Nd and Sm.

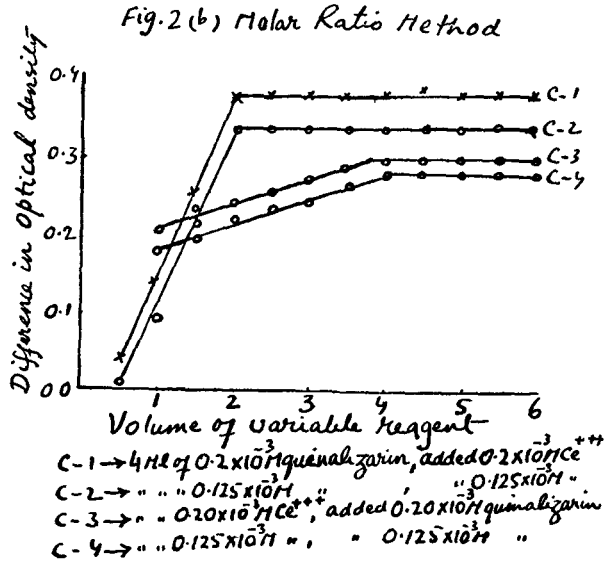

FIG. 2b

In the case of EBBR complexes for molar ratio method similar experiments were completed but the constant volumes of the rare-earths salts or the dye were 3 ml only.

The concentrations used in the molar ratio method were $0.25\times10^{-3}M$ and $0.2\times10^{-3}M$ for alizarin complexes, $0.2\times10^{-3}M$ and $0.125\times10^{-3}M$ in the case of quinalizarin complexes and 0.5×10^{-4} and $0.666\times10^{-4}M$ for that of EBBR complexes.

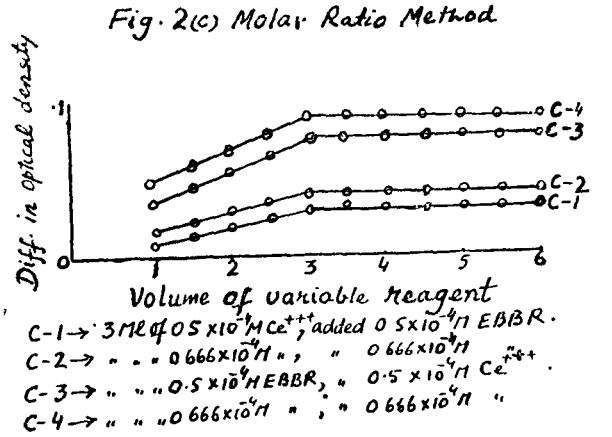

FIG. 2c

The apparent formation constants of the complexes of alizarin and quinalizarin were calculated by the method of Banerji and Dey[9] from Job's curves which were drawn with

9. S. K. Banerji and A. K. Dey, *Jour. Indian Chem. Soc.*, 1961, **38**, 139-46.

the optical density of the mixture as ordinate. The apparent formation constant of EBBR complexes were calculated from the Job's curves using the formula

$$K = \frac{x}{(a_1 - x)\ (b_1 - x)} = \frac{x}{(a_2 - x)\ (b_2 - x)}$$

where a_1, a_2, b_1 and b_2 were concentrations of the metal salts and EBBR at two points on two curves such that the optical density on them was the same.

DISCUSSION

Job's method yielded the combining ratio of 1 : 2 (metal-dye) for La, Ce, Pr, Nd and Sm complexes of alizarin and quinalizarin. The same ratio was confirmed by the two sets of molar ratio method. EBBR complexes with these metal salts gave a ratio of 1 : 1 (metal : EBBR). This ratio was verified by molar ratio methods.

The log of apparent formation constant for the complexes of EBBR with La, Ce, Pr, Nd and Sm was 5.2 ± 0.8. The various values of apparent formation constants calculated for the complexes of alizarin and quinalizarin differed markedly and no definite value could be determined for each complex.

Author's thanks are due to Prof. A. R. Kidwai for providing facilities to carry out these investigations.

CHEMISTRY DEPARTMENT,
ALIGARH MUSLIM UNIVERSITY,
ALIGARH,

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Nitroprusside Complexes of Silver(I), Mercury(II), Vanadium(IV), Yttrium(III), Lanthanum(III), Cerium(III), Praseodymium(III), Neodymium(III), Samarium(III), Gadolinium(III) and Dysprosium(III)

By Mohd. Mahfooz Khan and Naseer Ahmad

With 3 Figures

Summary

Sodium nitroprusside forms complexes with silver(I), mercury(II), vanadium(IV) and trivalent yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, and dysprosium. These interactions were studied using direct and reverse conductometric and in some cases direct potentiometric titrations. The complexes were isolated in the solid state and analysed. Formulae see page 111.

Inhaltsübersicht

Die Komplexbildung von Pentacyanonitrosoferrat, $[Fe(CN)_5NO]^{2-}$, mit Ag^{I}, Hg^{II}, VO^{2+} und den M^{III}-Ionen von Y, La, Ce, Pr, Nd, Sm, Gd und Dy wurde durch konduktometrische und potentiometrische Titration sowie praparative Isolierung der Komplexe (Formeln s. S. 111) untersucht.

Sodium nitroprusside reacts with the salts of cadmium, zinc and nickel[1]. With iron(III) sulphate and antipyrine it forms[2] $[Fe(C_{11}H_{12}ON_2)_3]_2 \cdot [Fe(CN)_5NO]_3$.

This communication is in extension of our previous work[3] on the nitroprusside complexes of Co(II), Ni(II), Cd(II), Zn(II), Cu(II), Mn(II), Fe(II) and Ti(III) and deals with our studies on the complexes of Ag(I) Hg(II), V(IV), Y(III), La(III), Ce(III). Pr(III), Nd(III) Sm(III), Gd(III), and

[1]) Chem. Abstr. **29**, 2873[1] (1935). G. Scagliarini, Atti IV Congr. naz. Chim. pura appl. (1932) 1933, 597—599; Chem. Abstr. **29**, 3622[9] (1935); G. Scagliarini and P. Montorte, Atti accad. Lincei **20**, 41—43 (1934); Chem. Abstr. **30**, 6670[1] (1936); G. Scagliarini, Atti Reale Accad. naz. Lincei **22**, 155 (1935).

[2]) Chem. Abstr. **46**, 3442[e] (1952); S. I. Gusev and R. G. Beiles, Ž. obšč. Chim. (J. gen. Chem. [UdSSR]) **21**, 1971 (1951).

[3]) M. M. Khan and Naseer Ahmad, Z. anorg. allg. Chem. **354**, 301 (1967).

Dy(III) with nitroprusside The formation of these complexes has been studied in aqueous solution using direct and reverse conductometric and in some cases direct potentiometric titrations The complexes were isolated as precipitates from aqueous solution or as crystals from solutions in methanol and analysed

Experimental

Aqueous solutions of La(III) Ce(III) Pr(III) Nd(III), Sm(III), and Y(III) were prepared from their chlorides (AEET. Bombay products), of Gd(III) and Dy(III) from their

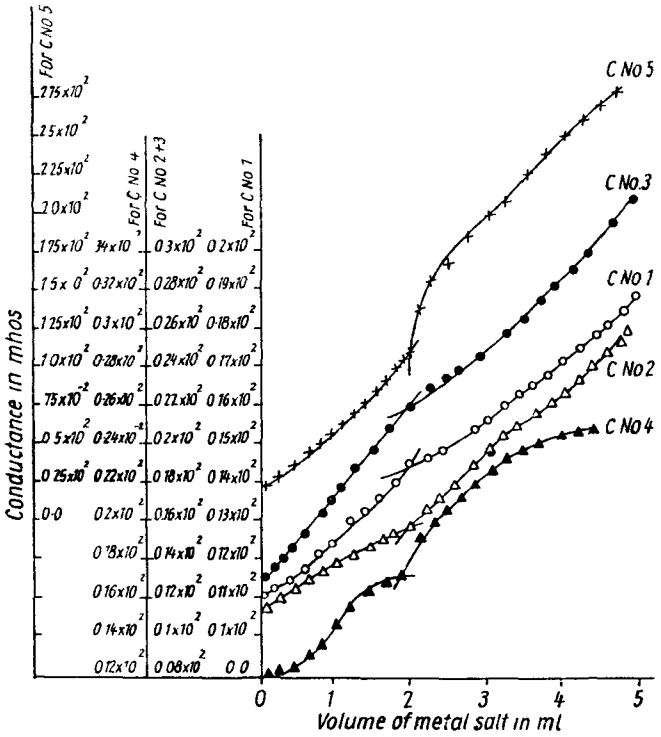

Fig 1 Conductometric titrations (reverse)·

C NO 1 $\frac{M}{200}$ $AgNO_3$ added to 40 ml of $\frac{M}{4000}$ Sodiumnitroprusside

C NO 2 $\frac{M}{50}$ $Hg(NO_3)_2$ added to 40 ml of $\frac{M}{1000}$ Sodiumnitroprusside

C NO 3 $\frac{M}{10}$ $LaCl_3$ added to 40 ml of $\frac{M}{200}$ Sodiumnitroprusside

C NO 4 $\frac{M}{40}$ $VOCl_2$ added to 40 ml of $\frac{M}{800}$ Sodiumnitroprusside

C NO 5 $\frac{M}{40}$ YCl_3 added to 40 ml of $\frac{M}{800}$ Sodiumnitroprusside

oxides (AEE. Bombay products) by first converting them into chlorides, of Hg(II) from its nitrate (B. D. H., A. R.), of Ag(I) from silver nitrate (E. Merck) and of VO^{+} from $VOCl_2$ (B. D. H.) The standard solution of silver nitrate was prepared by dissolving the required amount of the salt in conductivity water.

The solution of mercury(II) nitrate was standardized by precipitating it as HgS and weighing it as such[4]). The solution of vanadyl chloride was standardized by converting a

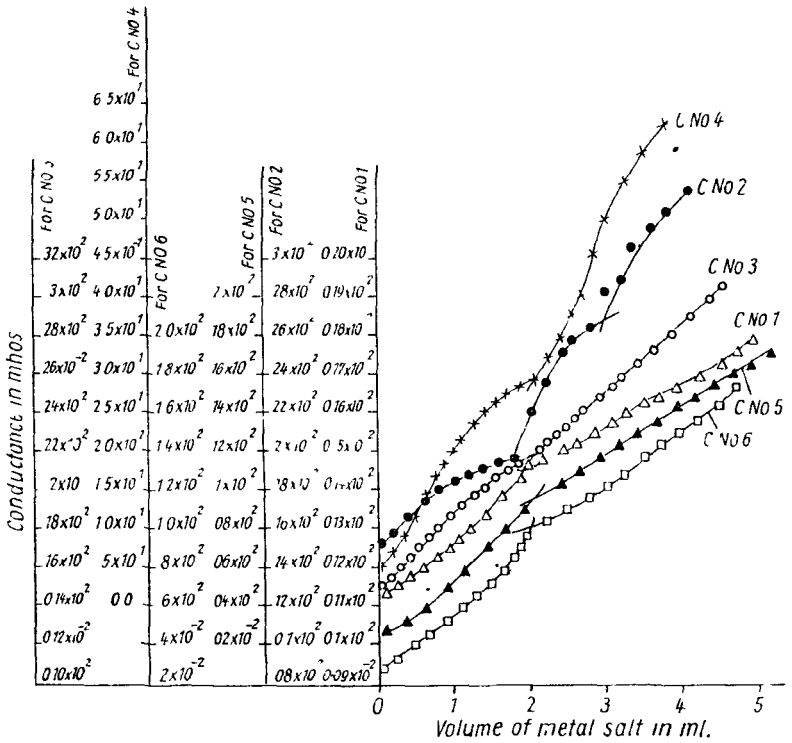

Fig. 2 Conductometric titrations (reverse)

C No 1 $\frac{M}{40}$ $CeCl_3$ added to 40 ml of $\frac{M}{800}$ Sodiumnitroprusside

C No 2 $\frac{M}{30}$ $PrCl_3$ added to 40 ml of $\frac{M}{600}$ Sodiumnitroprusside

C No 3 $\frac{M}{20}$ $NdCl_3$ added to 40 ml. of $\frac{M}{400}$ Sodiumnitroprusside

C No 4 $\frac{M}{20}$ $SmCl_3$ added to 40 ml. of $\frac{M}{400}$ Sodiumnitroprusside

C No 5 $\frac{M}{40}$ $GdCl_3$ added to 40 ml. of $\frac{M}{800}$ Sodiumnitroprusside

C No 6 $\frac{M}{40}$ $DyCl_3$ added to 40 ml. of $\frac{M}{800}$ Sodiumnitroprusside

[4]) N. H. FURMAN, Scott's standard Methods of Chemical analysis VI Ed. Vol. I, page 658 New York 1962.

known volume of it into vanadate, precipitating as mercurous vanadate, igniting and weighing as V_2O_5[5]. The strength of the rare earth solutions was determined by precipitating as oxalates. The oxalate was filtered through a sintered glass crucible and washed well with water. The crucible along with the precipitate was placed in a beaker containing dilute sulphuric acid and titrated against standard permanganate solution[6].

Direct and reverse conductometric titrations were performed using solutions of metal salts and nitroprusside in conductivity water. For measuring conductivity Philips Conductivity Bridge PR model 9500 was used (Fig. Nos. 1, 2 and 3).

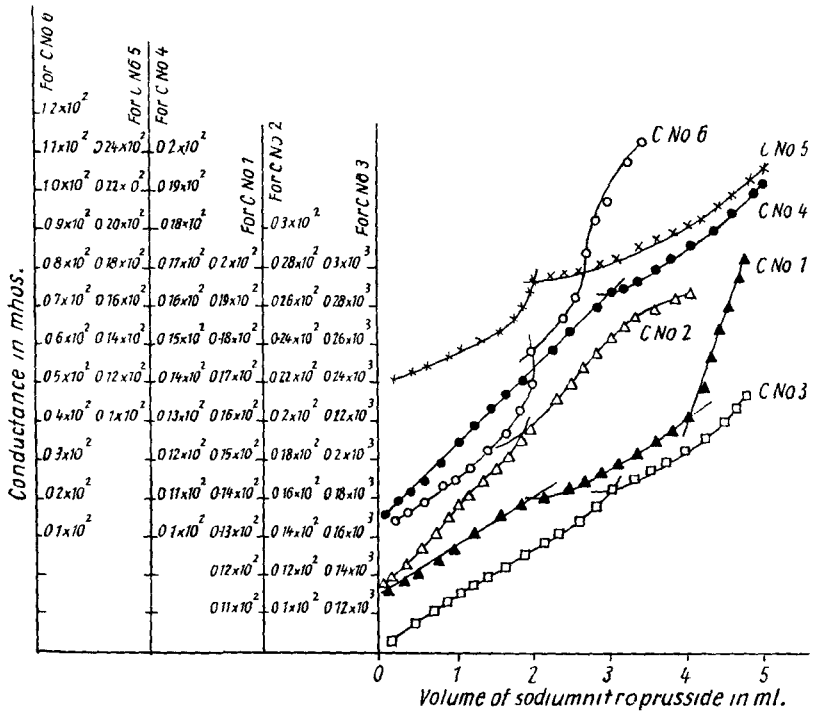

Fig. 3. Conductometric titrations (direct)

C.NO 1 $\frac{M}{100}$ Sodiumnitroprusside added to 40 ml of $\frac{M}{1000}$ $AgNO_3$

C.NO 2 $\frac{M}{40}$ Sodiumnitroprusside added to 40 ml of $\frac{M}{800}$ $Hg(NO_3)_2$

C.NO 3 $\frac{M}{40}$ Sodiumnitroprusside added to 40 ml of $\frac{M}{800}$ $LaCl_3$

C.NO 4 $\frac{M}{30}$ Sodiumnitroprusside added to 40 ml of $\frac{M}{600}$ $CeCl_3$

C.NO 5 $\frac{M}{40}$ Sodiumnitroprusside added to 40 ml of $\frac{M}{800}$ $PrCl_3$

C.NO 6 $\frac{M}{20}$ Sodiumnitroprusside added to 40 ml of $\frac{M}{400}$ $VOCl_2$

[5]) Cumming and Kay Quantitative chemical analysis 11th Ed. page 402 London.

[6]) G. L. P. Lundell and J. I. Hoffman Outline of methods of chemical analysis 8th printing, page 66, New York.

The potentiometric titrations were performed with the help of a Tinsley potentiometer using a lamp and scale outfit. Only direct titrations in the cases fo Ag, Hg, La, and Ce could yield any results.

The silver nitroprusside complex was obtained as a precipitate on mixing the aqueous solutions of silver nitrate and sodium nitroprusside in the molar ratio of 2:1. The precipitate was centrifuged, washed once with water and then repeatedly with 50% ethanol till the centrifugate was free from metal salt and nitroprusside. The precipitate was dried in a vacuum desiccator over quicklime for several days. The precipitate of mercury complex was obtained by heating the two reactants in the molar ratio of 1:1 in methanolic solution. The precipitate was washed with methanol. Gadolinium and Dysprosium chlorides and vanadyl chloride gave precipitates with sodium nitroprusside in methanol in cold. Chlorides of yttrium, lanthanum, cerium, praseodymium, neodymium and samarium in methanol were mixed with sodium nitroprusside in the same solvent in the molar ratio of 1:1 and heated on an water bath for about half an hour when shining small needle shaped crystals were produced. The crystals were washed with methanol an dried in a vacuum desiccator. The colour of vanadium complex in the wet state was green which changed to black on drying. The colour of the rest of the complexes in the wet state was almost pink. On drying the colour of the complexes of silver, mercury, praseodymium, gadolinium und dysprosium became light pink, of neodymium pink, of lanthanum and yttrium dirty pink, of cerium dark pink and of samarium light brown.

For analysis, a weighed quantity of the complex was fused with fusion mixture in a platinum crucible and dissolved in dilute nitric or some other acid.

From the solution of the fused complex in dilute nitric acid, silver was separated and estimated as AgCl and Iron was determined as ferric hydroxide.

The mercury nitroprusside complex was fused and dissolved in dilute hydrochloric acid from which mercury was separated as sulphide[4]) and iron was estimated as ferric hydroxide from the filtrate.

From the solution of fused vanadium nitroprusside complex in dilute nitric acid, iron was first separated as hydroxide[7]) with caustic soda and then vanadium estimated from the filtrate as V_2O_5.

The complexes of Y, La, Ce, Pr, Nd, Sm, Gd, and Dy were likewise fused and dissolved in dilute hydrochloric acid. The rare-earth elements were precipitated[6]) as oxalates with the help of ammonium oxalate, at a pH of 3—4 adjusted with the help of Bromothymol blue indicator. Iron was later on precipitated as hydroxide after destroying oxalate.

For the estimation of chloride, separate samples were used. The weighed amount of the complex was taken in a platinum crucible, carefully covered with fusion mixture and gently fused. The fused mass was dissolved in dilute nitric acid and chloride estimated as silver chloride.

For the determination of water, a weighed quantity of the complex was heated to 80 °C in an oven, dried in a vacuum desiccator over fused calcium chloride for several hours and reweighed. Microanalysis for the determination of carbon, hydrogen and nitrogen was done by Microanalytical service, Melbourne, Australia.

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[7]) Book in reference no. 4, page 532.

Results and Discussion

The direct and reverse conductometric titrations gave evidence for the formation of complexes in the ratio of 1:1 with all the eleven metal ions. There was a good indication of the formation of complexes in the ratio of 2:3 (metal nitroprusside) with lanthanum, cerium and praseodymium. In the case of silver, inflection points were observed at a molar ratio of 2:1 (Ag nitroprusside) in the curves of conductometric titrations. Potentiometric titrations confirmed this ratio for silver complex and yielded the ratio of 1:1 for the complexes of mercury, cerium and lanthanum.

The results are given in Table 1, where M stands for Ag, Hg, V, Y, La, Ce, Pr, Nd, Sm, Gd, Dy.

Table 1
Results of analysis (%)

	M	Fe	N	C	H	Cl	H_2O
$Ag_2[Fe(CN)_5NO] \cdot 2H_2O$	46.07	11.93	17.96	12.83	0.85		7.70
Observed	45.76	12.01	19.10	—	0.67	—	7.98
$Hg[Fe(CN)_5NO] \cdot 2H_2O$	41.32	12.33	18.57	13.26	0.89		7.95
Observed	41.15	12.29	18.54		0.91		8.01
$VO[Fe(CN)_5NO] \cdot 2CH_3OH$	11.67	16.08	21.22	21.22	2.37		
Observed	15.02	17.00	22.05	—	3.26	—	
$V[Fe(CN)_5NO]Cl \cdot 2CH_3OH$	22.01	13.80	20.78	20.78	1.98	8.77	
Observed	21.99	14.01	21.81	19.82	2.31	8.00	
$La[Fe(CN)_5NO]Cl \cdot 2CH_3OH$	30.58	12.28	18.49	18.49	1.76	7.81	
Observed	30.43	12.80	18.88	17.99	2.06	7.66	
$Ce[Fe(CN)_5NO]Cl \cdot 2CH_3OH$	30.76	12.25	18.44	18.44	1.75	7.79	
Observed	28.81	13.80	19.80	17.34	2.26	6.02	
$Pr[Fe(CN)_5NO]Cl \cdot 2CH_3OH$	30.87	12.22	18.42	18.42	1.75	7.78	
Observed	28.99	12.28	19.77	16.88	1.85	6.99	
$Nd[Fe(CN)_5NO]Cl \cdot 2CH_3OH$	31.38	12.12	18.28	18.28	1.74	7.72	
Observed	31.53	12.01	18.43	17.30	2.00	6.69	
$Sm[Fe(CN)_5NO]Cl \cdot 2CH_3OH$	32.28	11.98	18.04	18.04	1.71	7.62	
Observed	30.91	11.43	19.21	17.64	2.00	6.51	
$Gd[Fe(CN)_5NO]Cl \cdot 2CH_3OH$	33.27	11.80	17.77	17.77	1.69	7.51	
Observed	32.98	12.00	18.71	18.37	1.83	6.80	
$Dy[Fe(CN)_5NO]Cl \cdot 2CH_3OH$	34.01	11.67	17.59	17.59	1.67	7.42	
Observed	33.28	10.98	18.98	17.93	1.93	6.98	

The following formulae may be assigned to these complexes in aqueous solution and in the dry state.

in the dried state	in aqueous medium
$Ag_2[Fe(CN)_5NO] \cdot 2H_2O$	$NaAg[Fe(CN)_5NO] \cdot xH_2O$
	$Ag_2[Fe(CN)_5NO] \cdot xH_2O$
$Hg[Fe(CN)_5NO] \cdot 2H_2O$	$Hg[Fe(CN)_5NO] \cdot xH_2O$
$VO[Fe(CN)_5NO] \cdot 2CH_3OH$	$VO[Fe(CN)_5NO] \cdot xH_2O$
$M[Fe(CN)_5NO] \cdot 2CH_3OH$	$M'[Fe(CN)_5NO]Cl \cdot xH_2O$

where M stands for Y, La, Ce, Pr, Nd, Sm, Gd, and Dy.

where M′ stands for Y, La, Ce, Pr, Nd, Sm, Gd, and Dy.

$M''_2[Fe(CN)_5NO]_3 \cdot XH_2O$

where M″ stands for La, Ce and Pr.

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Novel Complexes of Uranium(V)

By J. Selbin,* N. Ahmad, and M. J. Pribble
(*Coates Chemical Laboratories, Louisiana State University, Baton Rouge, Louisiana* 70803)

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Novel Complexes of Uranium(V)

By J. Selbin,* N. Ahmad, and M. J. Pribble

(*Coates Chemical Laboratories, Louisiana State University, Baton Rouge, Louisiana* 70803)

Summary Several new complexes of formally quinquevalent uranium, all but one of which have the general formula UCl_5L_n, have been synthesized (the donor atoms in the organic ligands being N, P, As, S, Se, and Te) for which there is e.s.r. evidence suggesting that the lone U^V electron is strongly delocalized on to the unsaturated organic moiety, perhaps into π-antibonding MO's.

Uranium(V) chemistry has been confined to a very limited number and type of compounds because of the extreme instability of this oxidation state relative to the four and six states.[1] Apart from UX_6^- (X = F or Cl), there were only seven examples of complexes of the UX_5L type known until now, the only donor atoms in these compounds being halogen and oxygen.[2] We have extended the chemistry of uranium(V) to compounds containing ligands in which N, P, As, S, Se, and Te act as the donor atoms. The new compounds, listed in the Table, were characterized by elemental analyses (which support the stoicheiometries given), differential thermal analyses, magnetic susceptibilities (in cases where sufficient quantities were available for Gouy determinations), i.r., visible–u.v., and e.s.r. spectra.

The general preparative procedure for all of the new compounds is based upon the use as a starting material of UCl_5(tcac) the preparation of which we reported recently.[3] The ligand tcac, trichloroacrylyl chloride, $Cl_2C:CCl\cdot COCl$, co-ordinates to the U^V through the oxygen atom, but apparently so weakly that this ligand can be readily replaced by almost any other ligand, provided the latter does not react either with the tcac or with the U^V in a redox manner.

The UCl_5 tcac is dissolved in benzene, the solution is filtered, and then a benzene solution containing the ligand (in a 3 : 1 ligand : UCl_5 tcac mole ratio) is added with stirring. Immediate reaction occurs, the red colour of the UCl_5 tcac solution fading as a coloured precipitate deposits. Stirring is continued for several hours, followed by filtration and washing with benzene and CCl_4 or hexane. No recrystallization has been possible so far with any of the products since

they are either insoluble in common organic solvents or dissolve with decomposition. They are dried *in vacuo* and stored under dry argon or nitrogen. All the preparative work and subsequent manipulations of these compounds must be carried out with rigorous exclusion of both oxygen and moisture.

4—60 Gauss. The extreme broadness of the signal in the complexes which have bands with no low-lying empty antibonding MO's suggests that the lone electron is very much confined to a highly localized 5*f*-orbital. The narrow signal in the case of the new complexes, plus the free-electron *g* value, suggests that the lone 5*f*-electron of the

TABLE

New uranium(V) *Compounds*[a]

Compound	Colour	M.p.	corr μ_{eff}	$<g>$[b]
UCl_4(pyrazine)$_2$	Yellow	133dec.	2·04	2·000
UCl_4(phthalazine)$_2$	Orange	230dec.	2·25	2·006
UCl_4 phenazine	Red-brown	215dec.	—	2·006
UCl_4 bipy	Gray	—	—	2·054
UCl_4Ph_3P	Med. green	>300[c]	—	2·008
UCl_4 diphos	Pale green	>300[d]	2·70	2·022
UCl_4Ph_3As[e]	Green	—	—	—
$[UCl_4(PhS)]_2$[f]	Gray	104dec.	—	1·990
$UCl_4PhSeSePh$	Yellow	57dec.	3·1	2·005
$UCl_4PhTePh$	Violet-black	151dec.	2·84	2·057
Pr_4NUCl_8[g]	Golden yellow	—	—	1·963
UCl_4 tcac[g]	Orange-red	147—149[h]	1·54	1·990
UCl_4SOCl_2[g]	Red-orange	—	—	1·106

[a] Abbreviations are: bipy = 2,2′-bipyridyl; diphos = ethylenebis(diphenylphosphine).
[b] All e.s.r. spectra had to be run on powdered samples.
[c] Starts to darken at 140°, becomes very dark at 242°.
[d] Darkens above 200°.
[e] Analyses indicate there are impurities in this compound, but it forms in the same way, has the same appearance as, and gives an optical spectrum like that of the analogous Ph_3P compound.
[f] Presumed to be a dimer due to its insolubility and the double signal found in the e.s.r. spectrum
[g] Ref. 2. The $SOCl_2$ compound was reported earlier by H. Hecht, G. Jander, and H. Schlopmann, *Z. anorg. Chem.*, 1947, **254**, 255
[h] Sealed-tube values.

The structures are not yet known for any of these new complexes, but presumably the U^V retains six-co-ordination in most of them although seven-co-ordination cannot be ruled out in certain cases, such as UCl_4 diphos, UCl_4 bipy, and the pyrazine and phthalazine compounds. In both the diphos and Ph_3P compounds, i.r. spectra rule out P–H bonds (no bands in the 2400 cm.$^{-1}$ region) and P=O bonds (no strong bands in the 1050—1100 cm.$^{-1}$ region not present in the free non-oxy-ligand). Thus we believe U–P bonds are indeed formed here, and not phosphonium salts or phosphine oxide compounds.

The most interesting results to be obtained so far for these compounds are from their e.s.r. spectra. We have already reported[2] the first e.s.r. spectra for U^V compounds (all as powders) three of which are listed last in the Table, and found the average *g* values to be *ca.* 1·1 (with sign indetermined). The signals were extremely broad (*ca.* 200 Gauss). Yet for all of our new compounds, which have ligands containing aromatic systems, we find the average *g* values very close to the free-electron value, and furthermore the line-widths are quite narrow, ranging from

free U^V has been heavily delocalized on to the ligands and may spend (on the average) a great deal of time in the delocalized antibonding MO's of these molecules. The optical spectral data, to be reported later in a full paper and to be compared there with the previously obtained spectral data on U^V complexes,[2] support the idea that such delocalization is taking place. Indeed, there is a striking correlation between the clarity and detail of the optical spectra and the width of the e.s.r. signal. The smaller this width, the less clear and fewer in number are the optical bands. The optical spectra rule out all but trace amounts of U^{IV} compounds, and the analytical data and e.s.r. spectra as well as mode of formation, support the formulation of these products as U^V compounds despite some seemingly incongruous magnetic susceptibility data. These matters will be dealt with in more detail in the full paper.

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[c](*Received, May 13th*, 1969; Com. 671.)

[1] J. Selbin and J. D. Ortego, *Chem. Rev.*, 1969, **69**, in the press.
[2] J. Selbin, J. D. Ortego, and G. Gritzner, *Inorg. Chem.*, 1968, **7**, 966.

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STUDIES ON VANADYL SULPHATE COMPLEXES WITH HETEROCYCLIC AMINES

M. M. KHAN, N. AHMAD and A. U. MALIK

Prince of Wales Chemical Laboratories,
Aligarh Muslim University, Aligarh, India

PERGAMON PRESS

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involving the elimination of SiH_4 from solvated polysilicon units It would have to be assumed that these reactions were fast enough to allow fairly rapid formation of $KSiH_3$ according to Morrison and Ring s second stage (equation (2)) It seems equally possible, however, that the most important base catalyst for the elimination of SiH_4 is SiH_3^- initially produced as suggested by Morrison and Ring Neither of these suggestions accounts for the observed combining ratio and the end-point of 4 1 for Si KH The experiments with GeH_4 and with SnH_4 taken with the conductivity data in the table suggest to us that the anionic species present in solution is probably more complicated than indicated by the formula MH_3^- (M=Si, Ge or Sn)

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University Chemical Laboratory
Lensfield Road
Cambridge
England

N A D CAREY
E A V EBSWORTH†

*Present address Organisch Chemisch Instituut T N O Croesestraat 79 Utrecht Holland
†Present address Department of Chemistry, University of Edinburgh, Westmains Road Edinburgh

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Studies on vanadyl sulphate complexes with heterocyclic amines

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DURING the last two decades, extensive work has been carried out on Oxovanadium (iv) complexes [1, 2] Complex formation with Nitrogen containing ligands is of more recent discovery but a large number of papers have appeared on V(iv)-heterocyclic amine complexes[3–6] These studies are mainly concerned with the spectral and magnetic interpretation of ligand field splitting[7, 8]

The present communication deals with the composition and structure of complexes formed by the interaction of $VOSO_4$ with heterocyclic amines

EXPERIMENTAL

Vanadyl sulphate (B D H) was used Solutions of the salt were prepared in doubly distilled water or methanol VO^{+2} was estimated by precipitating vanadium as mercurous vanadate and weighing as V_2O_5[9]

Pyridine (py), 2-picoline (2 pic), 3-picoline (3 pic), 4-picoline (4 pic), 2,4-Lutidine (2, 4 L), 2 6 Lutidine (2, 6 L), Quinoline (Q), and Isoquinoline (I Q) were all E Merck products and were distilled before being used Acridine (Ac) (B D H product) was purified by crystallising it from acetone

The potentiometric measurements were made with the help of a Tinseley potentiometer type 3387B in conjunction with a lamp and scale outfit using platinum and calomel as indicator and reference electrodes respectively

1 J Selbin, *Chem Rev* **65**, 153 (1965)
2 J Selbin, *Coord Chem Rev* **1**, 193 (1966)
3 Hans J Bielig and Ernst Bayer *Justus Liebigs Annln Chem* **584** 96 115 (1953)
4 H Funk, W Weiss and M Zeising, *Z anorg allg Chem* **296** 36 (1958) H Funk G Mohaupt and A Paul, *Z anorg allg Chem* **302**, 199 (1959)
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6 R L Dutta and S Ghosh *J Indian chem Soc* **44** 273 (1967) and the references therein
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The conductometric titrations were performed employing a Philips Conductivity Bridge Model PR-9500 with a dip type conductivity cell (cell constant 1 482)

Infrared spectra were recorded with a Perking–Elmer infra cord model 137B for the range 3–15 μ using KBr pellets whereas the spectra in the range 15–27 μ were recorded on Beckman IR 5A fitted with a CsBr prism using nujol mull as a mulling agent

Preparation of the complexes

About 0 5 g of $VOSO_4$ was dissolved in 5 ml of methanol (A R) with slight warming and subsequent addition of about 20 ml of tetrahydrofuran (T H F) The solution was treated with an excess of the amine in T H F when a precipitate formed The precipitate was centrifuged, washed several times with T H F and finally dried in vacuum desiccator over CaO

Analysis of the complexes

1 $VO(py)SO_4$ Calcd for $VO(C_5H_5N)SO_4$ V 21 1 N 5 8, SO_4 39 7 C 24 8 Found V 21 0 N 5 7 SO_4 40 0 C, 24 7

2 $VO(2\text{ pic})SO_4$ Calcd for $VO(C_6H_7N)SO_4$ V, 19 9, N, 5 5, SO_4, 37 5 C, 28 1 Found V, 19 9 N, 5 4, SO_4, 37 9 C, 29 0

3 $VO(3\text{ pic})SO_4$ Calcd for $VO(C_6H_7N)SO_4$ V, 19 9, N, 5 5, SO_4, 37 5 C, 28 1 Found V, 20 0 N, 5 8, SO_4, 38 0, C, 29 3

4 $VO(4\text{ pic})SO_4$ Calcd for $VO(C_6H_7N)SO_4$ V, 19 9, N, 5 5, SO_4, 37 5, C, 28 1 Found V, 19 5 N, 5 6, SO_4, 37 9 C, 28 8

5 $VO(2,4\text{ L})SO_4$ Calcd for $VO(C_7H_9N)SO_4$ V, 18 9, N, 5 2, SO_4, 35 6 C, 31 2 Found V, 18 9 N, 5 1, SO_4 35 8, C, 30 9

6 $VO(2,6\text{ L})SO_4$ Calcd for $VO(C_7H_9N)SO_4$ V, 18 9, N, 5 2, SO_4, 35 6 C, 31 2 Found V, 18 8 N, 5 1, SO_4, 35 9 C, 31 2

7 $VO(Q)SO_4$ Calcd for $VO(C_9H_7N)SO_4$ V, 17 5, N, 4 8, SO_4, 32 8 C, 37 0 Found V, 17 3 N, 4 6, SO_4, 32 8, C, 37 2

8 $VO(I\text{ Q})SO_4$ Calcd for $VO(C_9H_7N)SO_4$ V, 17 5 N, 4 8 SO_4, 32 8, C, 37 0 Found V 17 3 N, 4 7, SO_4, 32 9, C, 36 0

9 $VO(AC)SO_4$ Calcd for $VO(C_{13}H_9N)SO_4$ V, 14 9, N, 4 0 SO_4, 28 1 C, 45 6 Found V, 14 9 N 3 9 SO_4, 28 6 C, 46 0

DISCUSSION

Vanadyl sulphate form 1 1 complexes with all these amines All the complexes are bluish-green except that of Acridine complex which is yellow Except those of quinoline and isoquinoline all the complexes are water soluble and hydrolysed on standing

Both direct and reverse conductometric titrations were performed between vanadyl sulphate and the amines Ratios of 1 1 and 1 2 for VO^{2+} to amines were obtained in all cases, except acridine, where a ratio of 1 2 was obtained in each titration

The potentiometric titrations were carried out by utilising $VO^{2+} \rightleftharpoons VO^{3+} + e$ couple the pH of the vanadyl sulphate soln was maintained at 2 7 On the basis of the potentiometric studies formation of 1 1 complexes for lutidines and 1 2 complexes for pyridine, picolines and the other amines was inferred

The difference in the composition of complexes by conductometric and potentiometric methods and from chemical analyses of the solids must be due to the lower solubility of the 1 1 complex in the medium used The extra energy required for coordination of VO^{2+} to one more tertiary nitrogen (strong σ donor) of amine is probably compensated by solvation energy

The important data regarding the metal-amine coordination are obtained by considering the regions where ring CC, CN stretching vibrations (1450–1650 cm^{-1}) and CH out of plane deformation vibrations (700–800 cm^{-1}) take place[10–11] In the region 1450–1650 cm^{-1} it is found that two distinct changes occur on coordination, namely, a reduction in the number of bands, with no appreciable changes in frequencies, and an increase in intensities of the bands In the region 700–800 cm^{-1} the bands are shifted to higher frequencies and there is an increase in intensities

The changes in the ring (CC CN) stretching vibrations and C H out of plane deformation vibrations

10 N S Gill R H Nuttal D F Scaife and D W A Sharpp *J inorg nucl Chem* **18** 79 (1961)
11 A U Malik *J inorg nucl Chem* **29** 2106 (1967)

on coordination may be explained on considering the electron densities around the heterocyclic nitrogen of the amines. The electron density on the heterocyclic nitrogen increases with 2 and 4 monosubstitution and 2,4 and 2,6 disubstitution, on coordination there is a change in distribution around the metal and the heterocyclic nitrogen (strong σ donor and weak π acceptor) resulting in the increase in intensities and reduction in the number of bands. From the i.r. studies it may be infered that the greater the electron density on the heterocyclic nitrogen, on coordination, the greater is the increase in the intensities and reduction in the number of bands and stronger is the metal-nitrogen band.

The strong band observed at 965 cm^{-1} in all the coordinated amines is assigned to V–O stretching vibrations[12]. The constant position of the band may be due to constant charge distribution around the metal coordinated to the tertiary nitrogen of the heterocycline amine.

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Prince of Wales Chemical Laboratories
Aligarh Muslim University
Aligarh
India

M. M. KHAN
N. AHMAD*
A. U. MALIK

*Present Address: Chemistry Department, Lousiana State University, Baton Rouge, La 70803, U.S.A.

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A re-assessment of the isomeric cross-section ratio in ^{75}Ge

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THE MEASUREMENT of the isomeric cross-section ratio is important from a number of points of view. It can be used to study both the transfer of angular momentum in nuclear reactions and the spin dependence of the nuclear level density in the final nucleus via the spin cut-off parameter[1]. Secondly, neutron-excited nuclear isomers may be useful for the measurement of neutron energy when used as threshold detectors. In this laboratory we are interested in the measurement of the cross-section ratio for fairly short-lived isomers having half-lives between a few seconds and 1 min. One such isomer is ^{75m}Ge, which can be formed by the $^{75}As(n, p)\,^{75m}Ge$ reaction using 14·MeV neutrons. There have been two reported measurements of this isomeric ratio for 14 MeV neutrons which disagree considerably. The first measurement is by Fukuzawa[2], who obtains a value of $0{\cdot}40 \pm 0{\cdot}11$, and the second by Okumura[3], who obtains a value of $0{\cdot}855 \pm 0{\cdot}074$. It is the object of the present work to obtain an independent value of the cross-section ratio.

Samples of a few grams of spectrographically-pure arsenic trioxide were irradiated with fast neutrons from the D-T reaction produced by a 150 keV S.A.M.E.S. accelerator, the neutron flux being monitored by the associated particle technique. The experimental arrangements were such that the samples were irradiated with neutrons of energies between 14·3 and 14·7 MeV. A simplified decay scheme of ^{75m}Ge is shown in Fig. 1.

Measurements of the induced γ-ray activities were made with a scintillation spectrometer having a 3″ × 3″ NaI(Tl) crystal. The 136 keV isomeric transition γ-ray was measured after an irradiation

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Spectrophotometric Studies on Nitro-alizarin and Purpurin Complexes with some Rare-earth Salts

S.M.F. Rahman, Naseer Ahmad and Jamil Ahmad

Thorium sulphate, Uranyl sulphate, Gadolinium chloride and Dysprosium chloride react with 3-nitro-alizarin and purpurin (1 : 2 : 4-Trihydroxy anthraquinone) forming dark brown and red complexes, have been studied in continuation with our previous works[1], spectrophotometrically using Vosburgh and Cooper[2] method of wave length selection, Job's method[3] of continuous variation and molar ratio method of Yoe and Jones[4]. Complexes of Gadolinium and Dysprosium chlorides with that of Nitroalizarin and Purpurin were isolated, analysed and formulae suggested.

EXPERIMENTAL

Thorium sulphate (A.R. B.D.H.) and uranyl sulphate (Chemistry Division, Bhaba Research Centre, India) were used in preparing their solutions in ethanol. A known volume of Thorium sulphate was evaporated to dryness and dissolved in distilled water. Thorium was precipitated as oxalate, ignited, weighed as ThO_2 and the strength of the solution was calculated[5].

The strength of the uranyl sulphate[6] was determined by evaporating a known volume of its ethanolic solution to dryness, dissolving the residue in water, precipitating uranium as $(NH_4)_2$–U_2O_7, igniting and weighing as U_3O_8. The solutions of gadolinium and dysprosium were standardised as mentioned earlier[7].

Vosburgh and Cooper method of wave length selection was employed with $2\times10^{-4}M$, $1{\cdot}6\times10^{-4}M$ and $1\times10^{-4}M$ solutions of gadolinium and dysprosium chlorides.

Job's method of continuous variations was done with various concentrations as represented in the curves. (1a, 1b).

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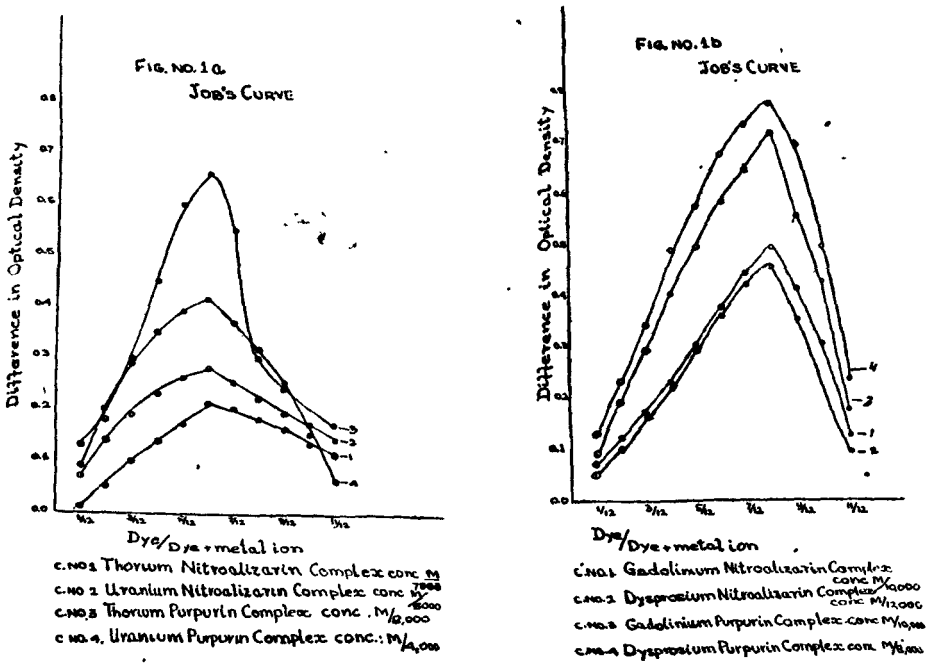
Molar ratio method was adopted to confirm the results of Job's method for this two sets of experiments were performed. In one set the volume of the metal ion was kept constant and varied amount of the dye was added, and in the second set of experiments the



volume of the dye was kept constant and varied amount of metal ions were added. Results were found to be in agreement with those obtained by Job's method. [Various concentrations of the solution were used as represented by the curves 2a, 2b, 2c and 2d.]

Lamberts and Beer's Law was found to hold good for 1 : 2, 1 : 3 and 1 : 4 (metal : dye) in the concentration range of $0{\cdot}33\times10^{-5}$—$4{\cdot}0\times10^{-5}M$, $0{\cdot}25\times10^{-5}$—$3{\cdot}0\times10^{-5}M$ and $0{\cdot}2\times10^{-5}$—$2{\cdot}5\times10^{-5}M$ for gadolinium and dysprosium complexes with purpurin. In the case of nitroalizarin complexes with gadolinium and dysprosium the validity of Lambert and Beer's Law was found to be in the conc. range of $0{\cdot}5\times10^{-5}$—$0{\cdot}8\times10^{-4}M$ for the ratio 1 : 2 (metal : dye).

The complexes of purpurin and nitroalizarin with that of gadolinium and dysprosium were prepared, and analysed as mentioned in our previous publications[1].

TABLE I

Results of Analysis
(*3-nitro-alizarin complexes*)

	Metal	C	H	N	Cl
1. *Gadolinium Complex* :					
Calculated for $(C_{14}H_6O_6N)_2$ GdCl	20.64	44.18	1.58	3.68	4.66
Value observed	20.62	44.00	1.76	3.66	4.65
2. *Dysprosium Complex* :					
Calculated for $(C_{14}H_6O_6N)_2$ DyCl	21.21	43.86	1.56	3.65	4.63
Value observed	21.22	43.81	1.72	3.64	4.62

TABLE 1 (*Contd.*)

Purpurin Complexes

1. *Gadolinium Complex* :					
Calculated for $(C_{14}H_7O_5)_2$ GdCl	22.20	47.83	1.99	—	5.07
Value observed	22.18	47.68	2.11	—	5.03
2. *Dysprosium Complex* :					
Calculated for $(C_{14}H_7O_5)_2$ DyCl	22.95	47.45	1.97	—	5.01
Value observed	22.92%	47.30	2.01	—	4.98

RESULTS AND DISCUSSION

Vosburgh and Cooper method exhibited maximum absorption at 520 mμ for nitroalizarin complexes of thorium, uranium, gadolinium and dysprosium and at 540, 575, 540 and 545 mμ for their purpurin complexes respectively. Job's method of continuous variations at the corresponding wave length of maximum absorption yielded a molar ratio of 1 : 1 for thorium and uranium complexes of purpurin and nitroalizarin. It gave a molar ratio of 1 : 2 (metal : dye) for the complexes of gadolinium and dysprosium with nitroalizarin and purpurin. These ratios were confirmed by two sets of molar ratio method. On the basis of the results of analysis the following formulae $(C_{14}H_6O_6N)_2$ GdCl, $(C_{14}H_6O_6N)_2$ DyCl, $(C_{14}H_7O_5)_2$ GdCl and $(C_{14}H_7O_5)_2$ DyCl may be suggested for nitroalizarin and purpurin complexes.

Department of Chemistry,
Aligarh Muslim University,
Aligarh.

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Studies on the complexes of chromium(II) chloride with some amino acids

Introduction

The complexes of transition metals with amino acids are of interest [illegible] of the biological importance of this family of compounds and the presence of [illegible] coordinating amino and carboxylic groups. Albert has carried out a detailed study on the stability constants of various amino acid complexes, based upon pH and potentiometric measurements. He showed that the reactivities of various amino acids towards a metal ion were dependent on the stability of the resulting complexes and ionization constants. However, no attempt has been made so far to study the amino acid complexes with unstable oxidation states. The present communication reports on the composition and stabilities of chromium(II) chloride complexes of some amino acids.

Experimental

The amino acids, glycine, L-proline, DL-serine, β-alanine, DL-α alanine, asparagine, L-leucine and DL-valine (B.D.H. biologically pure products) were [illegible]

and 0 01 *M* solutions were prepared in doubly-distilled, air-free water

Chromous chloride was prepared by the method of Bathis and Bailer[5] Chromic chloride was first reduced to chromous chloride with zinc–hydrochloric acid, and then precipitated as chromous acetate by adding ammonium acetate The red precipitate of chromous acetate was dissolved in a minimum quantity of hydrochloric acid The chromous chloride formed was precipitated with absolute alcohol, separated, and washed several times with small aliquots of ice-cold, air-free,doubly-distilled water It was then dissolved in doubly-distilled water and the solution kept in an air-tight storage vessel in an atmosphere of nitrogen (pH of solution, 3 5) The solution was standardized potentiometrically by titrating with standard copper sulphate.

Carbonate-free KOH was used for preparing the aqueous solution of KOH which was stored in a Pyrex bottle fitted with a tube containing KOH for protection against atmospheric carbon dioxide The solution was standardized by titrating with standard oxalic acid, and checked periodically before carrying out the pH-metric titrations

The potentiometric titrations were carried out using a Tinsley potentiometer with lamp and scale arrangements using platinum and calomel as indicator and reference electrodes, respectively. The pH-metric titrations were made with a direct reading EIL pH-meter, model 23A (England), using glass and calomel electrodes All titrations were carried out in a specially designed cell with provision for transferring the chromous chloride solution from the storage vessel and for passing oxygen-free nitrogen in order to stir the solutions The concentration of the chromous chloride solution was checked before the study of each system

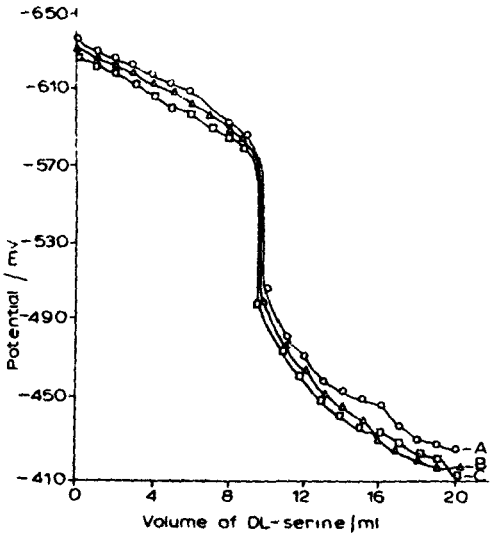

Fig 1 Potentiometric titrations (A) 10 ml 0 666 × 10 ⁻¹ *M* $CrCl_2$ (in cell) *vs* 0 666 × 10 ⁻¹ *M* DL-serine (from burette), (B) 10 ml 0 50 × 10^{-1} *M* $CrCl_2$ (in cell) *vs* 0 50 × 10 ⁻¹ *M* DL-serine (from burette), (C) 10 ml 0 44 × 10 ⁻¹ *M* $CrCl_2$ (in cell) *vs* 0 44 × 10 ⁻¹ *M* DL-serine (from burette)

Result and discussion

The composition of the complexes with amino acids was determined potentio-

metrically by taking various concentrations of chromous chloride (in the cell), and equimolar solutions of amino acids (from the burette). In all cases a ratio of 1 : 1 (chromium(II) : amino acid) was obtained from the potential–concentration curves (Fig. 1 for DL-serine). Information concerning complex formation was obtained from pH-metric titration curves. For each amino acid three sets of pH-metric titrations were carried out in the order: (*a*) amino acid (0.01 *M*), (*b*) chromous chloride (0.005 *M*), and (*c*) a mixture of chromous chloride and amino acid having a total concentration of 0.005 *M* and 0.01 *M* respectively, using 0.1 *N* KOH as titrant. The pH curves of all the amino acids show a definite shift indicating the formation of complexes of chromous chloride with amino acids (Fig. 2 for DL-serine).

The complex formation constant, K_c, was evaluated following the method of Albert[4]. The values of log K_c at $\bar{n} = 1$ (where n is the average number of molecules of amino acid bound by one atom of the metal) for various amino acids were calculated from the values of $-\log [Sc]$ obtained by the plot of $\bar{n}$ against $-\log [Sc]$ (Fig. 3), ([Sc] is the concentration of free amino acid). By application of relation (xii) of ref. 4

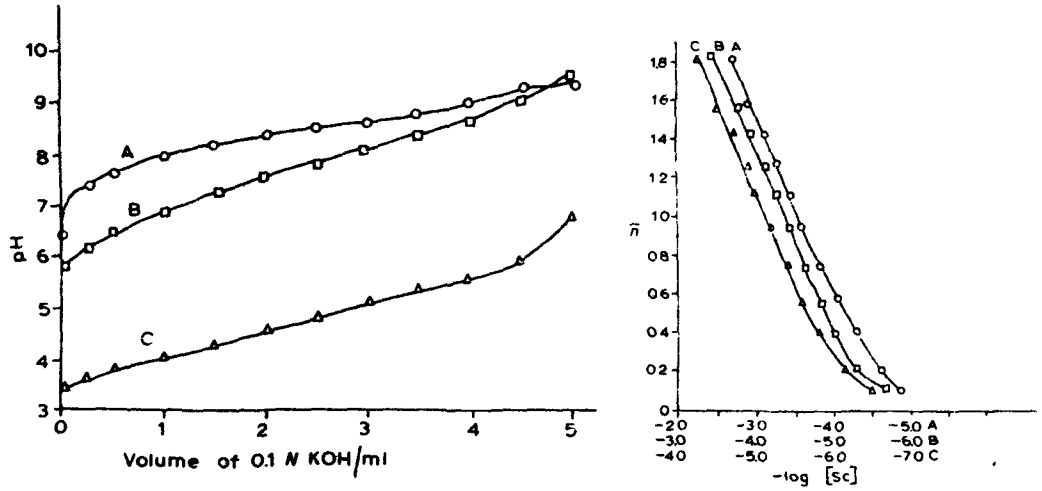

Fig. 2 pH-metric titrations (A) 50 ml 0.01 *M* DL-serine (in cell); (B) 25 ml 0.02 *M* DL-serine + 25 ml 0.01 *M* $CrCl_2$ (in cell). (C) 50 ml 0.005 *M* $CrCl_2$ (in cell).

Fig. 3. Formation curves. (A) DL-serine–chromium(II) complex, (B) DL-valine–chromium(II) complex, (C) DL-proline chromium(II) complex.

TABLE 1

	Graphically	*Calculated*
1. L-Asparagine	6.92	6.97
2. DL-α-Alanine	6.72	6.76
3. β-Alanine	9.86	9.89
4. Glycine	9.02	9.05
5. DL-Leucine	8.40	8.40
6. L-Proline	10.32	10.35
7. DL-Serine	7.20	7.21
8. DL-Valine	8.70	8.68

the values of log K_s for various amino acids were evaluated. The values obtained graphically and by calculation are given in Table 1.

The values of overall stability constants obtained from the formation curve (Fig. 3) are in good agreement with those calculated.

There does not seem to be any definite correlation between the nature of the amino acid and the K_s value; however, with a few exceptions the value of K decreases with increase in chain length of carbon atoms and also seems to decrease as the distance between amino and carboxylic groups increases. These observations could not be quantitatively substantiated as no information could be obtained as to the nature of the bounding because the complexes could not be isolated. The present studies are the first to report on the chemical reaction of unstable chromium(II) ions with amino acids, and the stabilities of the resulting complexes.

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Department of Chemistry,
Aligarh Muslim University,
Aligarh (India)

Omar Farooq
Anees Uddin Malik
Naseer Ahmad*

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* Present address: Chemistry Department, Louisiana State University, Baton Rouge, La 70803, (U.S.A.)

464 ELECTROANALYTICAL CHEMISTRY AND INTERFACIAL ELECTROCHEMISTRY
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SHORT COMMUNICATIONS

Studies on the composition and stability of uranyl, vanadyl and titanous complexes with some aminoacids

A number of papers on the metal complexes of amino acids[1-4] have appeared in the literature in recent years. These studies are mainly concerned with the determination of the stability constant of a complex by various electrometric methods, *viz.* potentiometry, pH-metry, polarography, etc. References to studies on the complexes of Cu, Zn, Fe, Ni, Co, Mn, Cd and other transition metals are available but no attempt has yet been made to investigate possible complex formation between VO^{2+}, UO_2^{2+} and Ti^{3+} ions with amino acids.

The present communication deals with the behaviour of these ions towards some amino acids. Formation of 1 : 1 complexes has been indicated by conductometric titrations, and the stability constants of the complexes have been computed from the results of pH-metric titrations.

Experimental

Amino acids such as glycine, β-alanine, DL-α-alanine, L-asparagine, DL-serine, L-leucine, DL-valine and L-proline (B.D.H. biologically pure) were used for the experiments, and their solutions (0.01 *M*) were prepared in doubly-distilled water.

Uranyl sulphate (B.D.H. AnalaR), and vanadyl sulphate (B.D.H.) were employed and solutions of these salts were analysed gravimetrically as the metal oxides[5,6]. An aqueous solution of titanium(III) chloride was prepared by dissolving crystals[7] of $TiCl_3 \cdot 6\,H_2O$ in air-free doubly-distilled water, and the solution standardized[8]. Fresh solutions were always prepared before use and kept covered with a layer of kerosene oil or toluene throughout the investigations to avoid oxidation.

Carbonate-free KOH solution was used for pH-metric titrations. It was stored in a Pyrex bottle fitted with a KOH tube for protection against atmospheric CO_2. The solution was standardized by titrating with standard oxalic acid solution, and the strength was checked periodically before carrying out pH-metric titrations.

The conductometric titrations were performed using a Philips conductivity bridge model PR 9500/90 and a dip type conductivity cell (cell constant 1.48). The pH-metric titrations were carried out with a direct reading EIL pH-meter model 23A using glass and calomel electrodes. All the titrations were carried out in a specially designed cell, with provision for adding metal salt solutions from a burette, to a stirred oxygen-free system.

Results and discussion

The composition of the vanadyl, uranyl and titanous complexes with various amino acids was determined conductometrically. The conductometric titrations were reversible. In all cases a ratio of 1 : 1 (metal : amino acid) was established. Typical curves are given in Fig. 1. The pH-metric titrations were performed in triplicate for each amino acid. The titrations were carried out in the order: (a) amino acid (0.01 *M*),

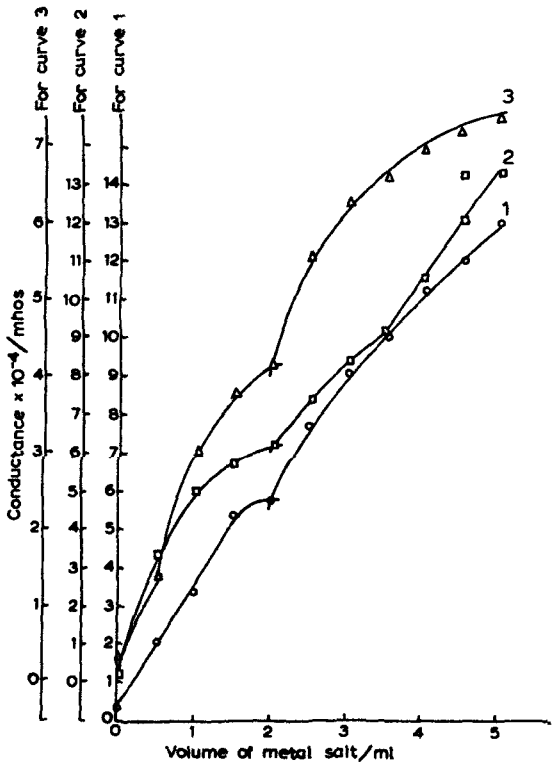

Fig. 1. Reverse conductometric titrations: (1) $M/15$ $TiCl_3$ added to 40 ml of $M/300$ DL-serine, (2) $M/12$ UO_2SO_4 added to 40 ml of $M/240$ DL-α-alanine, (3) $M/15$ $VOSO_4$ added to 40 ml of $M/300$ DL-valine.

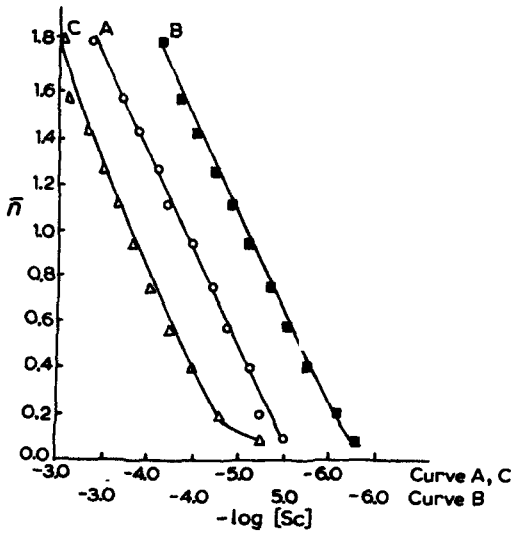

Fig. 2. Formation curves: (A) DL-valine–$VOSO_4$ complex, (B) DL-α-alanine–UO_2SO_4 complex, (C) DL-serine–$TiCl_3$ complex.

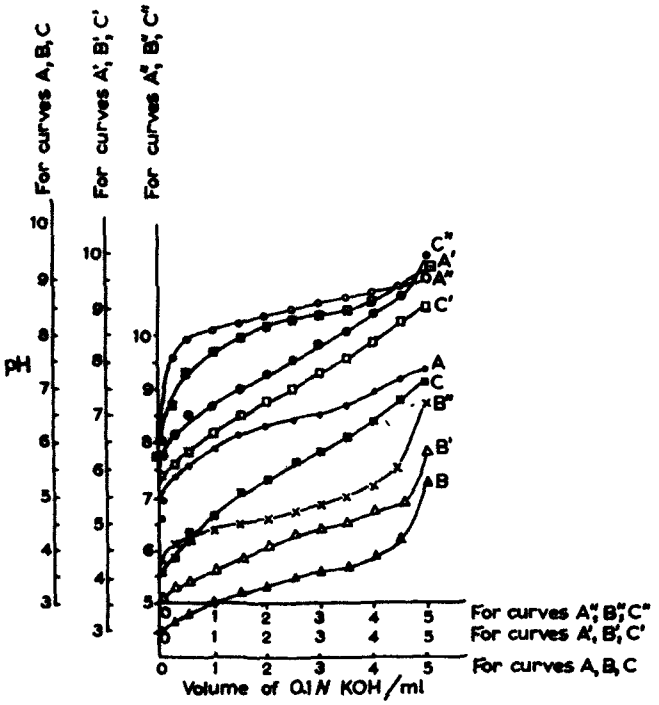

Fig. 3. pH-metric titrations: (A, B, C) DL-serine–$TiCl_3$, (A', B', C') DL-α-alanine–UO_2SO_4, (A", B", C") DL-valine–$VOSO_4$.

TABLE 1

VALUES OF LOG (K_s/mol^2 l^{-2}) FOR VANADYL, URANYL AND TITANOUS AMINO ACIDS COMPLEXES OBTAINED BY TWO METHODS

Amino acids	*Vanadyl sulphate*		*Uranyl sulphate*		*Titanous chloride*	
	Theo-retical	*Graphi-cal*	*Theo-retical*	*Graphi-cal*	*Theo-retical*	*Graphi-cal*
L-Asparagine	6.95	6.90	6.88	6.85	7.25	7.20
β-Alanine	9.77	9.80	9.92	9.90	9.72	9.70
DL-α-Alanine	8.75	8.70	9.00	9.00	8.53	8.50
Glycine	× ×	× ×	8.62	8.65	8.52	8.50
L-Leucine	9.08	9.10	8.61	8.60	8.55	8.50
L-Proline	10.33	10.30	10.46	10.45	10.08	10.05
DL-Serine	7.54	7.50	6.86	6.90	7.60	7.60
DL-Valine	8.65	8.65	8.59	8.60	8.12	8.20

(b) metal salt (0.005 *M*) and (c) metal salt and amino acid (total concentration 0.005 *M* and 0.01 *M*, respectively), employing 0.1 *N* KOH as titrant. The pH-titration curves show appreciable shifts, indicating the formation of complexes with the amino acid (Fig. 3). The complex formation constant K_s was evaluated by the method modified by Albert[4].

The values of log K_s at $\bar{n}=1$, where $\bar{n}$ is the average number of molecules of

amino acid bound by one atom of the metal ion, were calculated from the values of $-\log [Sc]$ obtained by plotting $\bar{n}$ *vs.* $-\log [Sc]$ (Fig. 2). [Sc] is the concentration of the free amino acid. The values of log K_s for various amino acids evaluated from the formation curves, and those calculated are given in Table 1.

The values of the overall stability constants log K_s obtained from the formation curves (Fig. 2), are in good agreement with those calculated.

Uranyl sulphate, vanadyl sulphate and titanous chloride form 1 : 1 complexes with various amino acids (L-asparagine, β-alanine, DL-α-alanine, glycine, L-leucine, L-proline, L-serine and DL-valine). In the vanadyl and titanous complexes the values of log K_s vary from L-asparagine (6.95, 7.25) to L-proline (10.33, 10.08), whereas in uranyl complexes the variation is from DL-serine (6.86) to L-proline (10.46). There does not seem to be any correlation between the nature of the aminoacids and the K_s values although, with a few exceptions, the latter decreases with increase in chain length of carbon atoms. The real nature of bonding in these complexes is a matter of speculation as no complex could be isolated in a sufficiently pure form.

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Department of Chemistry,
Aligarh Muslim University,
Aligarh (India)

Omar Farooq
A. U. Malik
N. Ahmad*
S. M. F. Rahman

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* Present address: Department of Chemistry, Louisiana State University, Baton Rouge, La. 70803, U.S.A.

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NEW COMPLEXES OF URANIUM(V)

J SELBIN, N AHMAD* and M J PRIBBLE†
Coates Chemical Laboratories, Louisiana State University, Baton Rouge, La 70803

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Abstract—Nineteen new uranium complexes, eighteen of which contain the element in the very unusual oxidation state of five, and one of which contains quadrivalent uranium complexed for the first time by an arsenic donor ligand, are reported The novel uranium(V) compounds include, for the first time, ligands whose donor atoms are nitrogen, phosphorus, arsenic, bismuth, sulfur, selenium and tellurium The compounds, all prepared under a strictly inert atmosphere, were characterized by elemental analysis, color, decomposition temperature, magnetic moment, ESR average g value (and signal width), i r spectroscopy and, in part, by NMR and visible, near i r, near u v spectroscopy, and mass spectrometry

INTRODUCTION

A RECENT comprehensive review of the chemistry of quinquivalent uranium reveals very few complexes of the metal in this unusual oxidation state[1]. The only compounds which have been studied are salts of UX_6^- (X = F^-, Cl^-, Br^-, I^-) (see Ref. [1]) and UOX_5^{2-} ($X = F^-$, Cl^-, Br^-)[2]; and seven so-called "addition" compounds of the UX_5L type (where X = Cl, $L = PCl_5$, $SOCl_2$, Ph_3PO, $(C_8H_{17})_3PO$, or TCAC‡; and X = Br, $L = Ph_3PO$ or hexamethylphosphoramide) (see Ref. [1]). Thus, only halide ions and oxygen donor ligands had been found complexed to U(V) until we prepared a series of new compounds, some which were reported in a recent preliminary communication[3]. We report here the preparative procedures used to obtain the new products and some of the more pertinent physical properties of the compounds.

EXPERIMENTAL

All preparations were carried out in a dry box having a continuously circulated atmosphere of rigorously dry and oxygen-free nitrogen Absolutely dry, deaerated reagent grade or better solvents and ligands were employed The starting material for all of the new complexes is UCl_5 TCAC‡, the preparation of which we have already described elsewhere[4] This reddish-orange crystalline compound is quite soluble in benzene and so benzene was most often used as the solvent medium for reaction between the dissolved UCl_5 TCAC and the ligand This very unusual addition compound appears to be the key to our success in preparing so many and such a variety of new U(V) compounds We have some evidence that dissolution of UCl_5 TCAC in benzene occurs with at least partial decomposition of the addition compound, not surprising since acid chloride molecules are known to be extremely poor ligands Thus it is possible that the actual reaction with a given ligand and our benzene solution of UCl_5 TCAC occurs with UCl_5, or more likely the known dimer, U_2Cl_{10}, which would

*On study leave from Aligarh Muslim University, Aligarh, India
†Present address Department of Chemistry, Limestone College, Gaffney, South Carolina
‡TCAC = trichloroacryloylchloride, $Cl_2C = CClCOCl$

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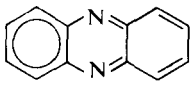
be expected to result after the detachment of the weakly coordinated acyl chloride In any case, the important point is that the benzene solution of UCl_5 TCAC has served as the starting point for the preparation of compounds of U(V) containing, for the first time, ligands which coordinate through N, P, As, (Sb) Bi, S, Se, and Te atoms

Compounds containing N-donor ligands

1 *Pentachloro(phenazine)uranium(V)*, UCl_5(phenazine) The ligand,



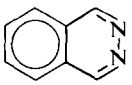
dissolved in benzene was added to a benzene solution of UCl_5 TCAC, in a mole ratio of approximately 2 1 A precipitate formed immediately and the entire mixture was stirred for about 30 min and then the solid separated by centrifugation The residue was washed several times with benzene, each time separating the solid by centrifugation and discarding the liquid This washing procedure was then repeated 2–3 times using *n*-hexane The solid was then dried under vacuum for 24 hr Differential thermal analysis (DTA) shows small endothermic peaks at 215° and 302° and a large endothermic peak at 319°C

The results of elemental analyses are collected in Table 1 for this as well as all other new compounds

2 *Pentachlorobis(pyrazine)uranium(V)*, $UCl_5(pyrazine)_2$ The ligand,

dissolved in benzene was added to a benzene solution of UCl_5 TCAC, in a mole ratio of approximately 2 1 The remainder of the procedure follows exactly that for the phenazine compound DTA shows endothermic peaks at 133° and 272°C The compound changes color at ~120° and melts with decomposition at 133°C It is soluble in nitromethane and acetonitrile

3 *Pentachlorobis(phthalazine)uranium(V)*, $UCl_5(phthalazine)_2$ The ligand,



dissolved in benzene was added to a benzene solution of UCl_5 TCAC, in a mole ratio of approximately 2 1 The remainder of the procedure follows exactly that for the phenazine compound DTA shows endothermic peaks at 230°, 272°, and 328°C The compound is soluble in CH_3CN and CH_3NO_2, but insoluble in $CHCl_3$ and CH_2Cl_2

4 *Pentachlorobis(pyridine)uranium(V)*, $UCl_5(py)_2$ Reagent grade pyridine was distilled from CaH_2 in an inert atmosphere Then a pyridine–benzene mixture was added to a benzene solution of UCl_5 TCAC until no more precipitate formed The supernatant liquid was decanted after several min of stirring and then the washing, separation, and drying was carried out as described for the phenazine compound The compound is soluble in CH_3NO_2 and CH_3CN, but these solutions are not stable for more than about 2 hr

5 *Pentachlorobis(o phenanthroline)uranium(V)*, $UCl_5(ophen)_2$ Reagent grade *o*-phenanthroline was recrystallized from dry benzene and then heated at its melting point under vacuum for 16 hr to remove all water Thermogravimetric analysis did not reveal any loss in weight due to water, and the dried ligand melted at 115–116 5° The ligand dissolved in benzene was then reacted with a benzene solution of UCl_5 TCAC, in a mole ratio of 2 1 Isolation, washing and drying of the product followed procedures described above for the phenazine compound The compound is insoluble in CH_3NO_2 and CH_3CN

6 *Pentachlorobis(2-mercaptopyridine)uranium(V)*, $UCl_5(2\text{-mcpy})_2$ The ligand was recrystallized from benzene and then the reaction carried out in benzene solution and the product isolated as previously described This compound changes color at 140° and melts with decomposition at 144°C It is soluble in both CH_3NO_2 and CH_3CN

7 *Pentachlorodi[ethylenebis(salicylaldimine)]uranium(V)*, $UCl_5(enbissal)_2$ The quadridentate

Schiff's base ligand enbissal was prepared in the usual way by reaction of anhydrous ethylenediamine with salicylaldehyde in an approximate 1 2 mole ratio The purified product was dissolved in benzene and added to a benzene solution of UCl_5 TCAC The blackish-green product was isolated as previously described There is stoichiometric as well as ir evidence (*vide infra*) that the ligand has lost neither of its acidic protons and is coordinated to the uranium as a neutral molecule The compound is very sensitive to oxygen and moisture and DTA was not possible It dissolves with almost immediate decomposition in $CHCl_3$ and CH_2Cl_2, and it is slightly soluble in CH_3NO_2 and CH_3CN

8 *Tetrachloromono(2 2 dipyridyl)uranium(V)chloride* $[UCl_4dipy]Cl$ Anhydrous reagent grade ligand, dipy was dissolved in benzene and added to a benzene solution of UCl_5 TCAC in approximately a 3 1 mole ratio The yellow product was isolated by filtration and washing followed by vacuum drying overnight The formulation of this compound as a 1 1 electrolyte is based upon its equivalent conductance (*vide infra*) in nitromethane solution At 205° the yellow compound turned brown and at 215° white crystals appeared on the surface of the dark solid At 270° the dark solid melted

9 *Pentachlorobis(8-hydroxyquinoline)uranium(V)*, $UCl_5(oxine\ H)_2$ Approximately 1 7 mole of UCl_5 TCAC was dissolved in 60 ml of benzene and 3 mole of pure 8-hydroxyquinoline added to the solution An immediate reaction occurred and a dark brown, finely divided precipitate formed The reaction mixture was stirred overnight and then the solid separated by filtration, washed with CCl_4 and dried in vacuum The compound is extremely air and moixture sensitive and it is decomposed by solvents, preventing the preparation of any solutions When it was heated under vacuum a light colored solid sublimed at about 120° leaving a residue slightly lighter in color than the original compound Under normal pressure the compound appeared to decompose at about 200° and the dark residue did not melt below 300°

10 *Pentachlorotetrakis(8-hydroxyquinoline)uranium(V)* $UCl_5(oxine\ H)_4$ A solution containing *ca* 2 mole of UCl_5 TCAC in 40 ml of benzene was prepared and to this was added a benzene solution containing 8 1 mole of oxine An immediate reaction ensued producing a finely divided brown precipitate The mixture was stirred overnight in an attempt to increase the particle size prior to filtration The brown precipitate was filtered, washed with benzene and vacuum dried When dry the compound is tan It turns dark reddish-brown at 230° but does not melt below 300° The compound is extremely air and moisture sensitive, decomposed rapidly by most solvents, although a nitromethane solution proved to be stable long enough to allow a conductance measurement to reveal that no ions are produced in this solvent by simple dissolution

Compounds containing P-*donor ligands*

11 *Pentachloro(triphenylphosphine)uranium(V)* $UCl_5(Ph_3P)$ The ligand 4 6 m mole Ph_3P was dissolved in 25 ml of benzene and this was added to a benzene solution containing ~2 4 m mole of UCl_5 TCAC Immediate loss of the red color of the latter solution and the formation of a fluffy light green precipitate signalled a rapid reaction The mixture was stirred for about 10 min the precipitate washed by decantation with benzene, then filtered and washed with several small portions of benzene and dried in vacuum The medium green product was found to be insoluble in non-polar solvents and decomposed by many others It is slightly soluble in nitromethane and conductance measurements in this solvent show that the compound does not ionize The compound begins to darken at about 140° appears "wet" at 190°, becomes very dark at 242°, but does not melt below 300°

12 *Pentachloro{ethylenebis(diphenylphosphine)}uranium(V)*, $UCl_5(EBDPP)$ A benzene solution of the ligand, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$, was prepared, containing 3 1 m-mole in 25 ml benzene This was added to a solution containing 2 m mole UCl_5 TCAC in 35 ml benzene and an immediate reaction occurred which produced a green precipitate After 15 min of stirring the product was separated by filtration, washed with benzene and dried overnight in vacuum The dry compound is a very pale green powder which is insoluble in nonpolar solvents and decomposed by most others It is slightly soluble in nitromethane, in which it exhibits zero conductance, suggesting that it is not ionized in that solvent The compound darkens when heated to 200°, but does not melt below 300° Differential thermal analysis showed no peaks (endothermic or exothermic) up to 500°[1]

Compounds containing As- Sb *and* Bi-*donor ligands*

13 *Tetrachlorouranium(V) μ dichloro trichloro (triphenylarsine)uranium(V)chloride*[5] $[U_2Cl_{\text{-}}$

5 This name must be considered tentative only since it is based upon a presumed structure for which there is inconclusive although suggestive evidence (*vide infra*)

Table 1

	Compound*	Color	Elemental analyses† C	H	N	U	Cl	Other (X)	Decomposition temp (°C)	corr μ_{eff}	$<g>$	Signal width (Gauss)
1	UCl_5(phenazine)	Red-brown	24 20	1 35	4 70		29 77		215		2 006	25
			26 67	1 88	4 04		30 64					
2	UCl_5(pyrazine)$_2$	Yellow	16 70	1 40	9 74		30 80		133	2 04	2 000	13
			17 53	2 01	9 01		30 6					
3	UCl_5(phthalazine)	Orange	28 45	1 79	8 29		26 24		230	2 28	2 006	7
			27 14	2 42	7 57		25 48					
4	$UCl_5(py)_2$	Brown	20 94	1 76	4 88		30 91		146–148	2 74	2 004	11
			21 04	1 85	4 74		32 48					
5	UCl_5(ophen)$_2$	Yellow	37 16	2 08	7 22		22 85		>330	2 86	2 006	15
			37 41	2 61	7 15		22 59					
6	UCl_5(2 mcpy)$_2$	Pale yellow	18 84	1 58	4 39		10 06	27 80 (S)	144	2 68	2 004	16
			20 33	1 80	4 39		9 76	27 61				
7	UCl_5(enbissal)$_2$	Blackish-green	40 37	3 38	5 88		18 62		116–119	3 77		
			39 80	3 76	5 97		18 63					
8	[UCl_4(dipy)]Cl	Yellow	21 02	1 41	4 82	41 65			(c)	2 78	2 005	15
			22 42	1 98	4 98	40 13						
9	UCl_5(oximeH)$_2$	Dark brown	30 68	1 86			25 15		200	1 95	2 001	15
			30 67	2 61			22 94					
10	UCl_5(oximeH)$_4$	Tan	43 39	2 83	5 66	23 89	17 79		‡	2 84	2 286	1124
			42 80	2 88	5 69	24 99	17 15					
11	$UCl_5(Ph_3P)$	Green	31 91	2 23		35 13		4 57 (P)	‡		2 008	25 5
			31 90	3 03		36 22		3 95				
12	UCl_5(EBDPP)	Pale green	38 37	2 97		29 25	21 79	7 61 (P)	‡	2 76	2 022	39
			38 18	3 30		28 68	20 43	6 77				
13	[$U_2Cl_4(Ph_3As)$]Cl	Pale green	19 02	1 33		41 88		6 59 (As)	‡	3 40		
			20 60	2 07		42 41		7 97		1 70/U^{5+}	1	
14	UCl_4(diars)	Light yellow	18 14	1 83			21 42	22 64 (As)	236			
			18 17	2 95			20 68	21 48				
15	[$U_2Cl_4(Ph_3Bi)$]Cl	Pale green	16 99	1 92					‡		2 005	7 2
			15 19	1 41								
16	UCl_4T 4HT	Black	42 45	2 95		24 06	14 33		207	1 94	1 980	>2000
			43 80	3 54		24 22	13 84		‡			
17	[UCl_4(PhS)]$_2$	Gray	14 74	1 03		48 68	28 99		104		1 990	2 and 30
			15 21	1 28		48 67	27 98					
18	UCl_5(PhSeSePh)	Yellow	19 81	1 39			24 37	21 71 (Se)	57	3 1	2 005	4
			19 32	1 78			23 84	21 17				
19	UCl_5(PhTeTePh)	Violet-black	17 48	1 22			21 49	30 94 (Te)	151	2 84	2 007	18
			17 09	1 43			20 27	30 32				

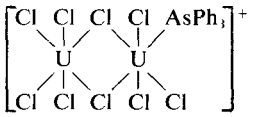
*The compounds are listed in the order in which their preparation has been described For the meaning of the abbreviations used for certain ligands, see that section of the experimental part

†The first listed value under each element is the percentage which is theoretical for the compound, the second value is the observed percentage

‡For details see the experimental section where the preparation of the compound has been given.

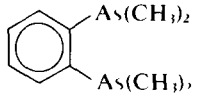
$(Ph_3As)]Cl$ Preparations of this compound using benzene as the solvent gave poor yields (for reasons unknown to us) and so toluene was later employed as the solvent A toluene solution of UCl_5 TCAC, 1 5 m mole in 40 ml, was prepared It has the same deep red color characteristic of the benzene solutions To this was added a solution of pH_3As prepared by dissolving 4 4 m mole of the ligand in 25 ml of toluene An immediate reaction produced a light green precipitate The reaction mixture was stirred overnight, filtered and the solid washed with benzene The product appears to be the same whether the reaction mixture is filtered after 3 hr or after 20 hr On heating, the pale green color changes to light brown at about 130° It appeared that some portion of the compound had volatilized at this temperature (probably Ph_3As) The color deepened at 190° and the dark brown residue did not melt below 300°

The equivalent conductance of a $7\ 1\times10^{-5}$ M solution of this compound in nitromethane was 86 mhos The equivalent conductance of a $1\ 2\times10^{-3}$ M solution of $(C_2H_5)_4NI$ in nitromethane is 104 mhos cm^2 Thus the evidence supports our postulate of a 1 1 electrolyte, presumably $[U_2Cl_9(Ph_3As)]Cl$ The most likely structure for such a cationic species consistent with the six coordinate geometry common for U(V) is with each uranium octahedrally coordinated We believe that the



reason for the stoichiometry of one Ph_3As to two UCl_5 arises from the great insolubility in benzene of the 1 1 salt which forms as soon as one chloride has been displaced from the neutral dimer U_2Cl_{10} There is thus no opportunity afforded a second ligand molecule to attach to the uranium The stoichiom etry of a product obtained from UCl_5 TCAC in benzene reacting with Ph_3Sb in benzene approaches $2UCl_5\ 1Ph_3Sb$, but we could not obtain the product pure We believe it to be contaminated with the dimer, U_2Cl_{10} However, the product obtained when Ph_3Bi was the ligand used does have the stoichiometry $2UCl_5\ 1Ph_3Bi$ (*vide infra*)

14 *Tetrachloro{o phenylenebis(dimethylarsine)}uranium(IV)*, UCl_4(diars) The reaction in benzene between dissolved UCl_5 TCAC and the diars ligand, produced a light yellow, very unstable

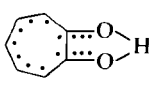


and air sensitive product which from all evidence we have been able to gather, appears to be a com plex of *tetravalent* uranium It melts with decomposition at 243°C and turns black It is insoluble in CH_3CN CH_3NO_2, CCl_4, $CHCl_3$, CS_2, and CH_2Cl_2

15 *Tetrachlorouranium(V)-μ-dichloro-trichloro(triphenylbismuthine)uranium(V)chloride* $[U_2Cl_4(Ph_3Bi)]Cl$ To a solution containing ~1 5 m-mole UCl_5 TCAC in 25 ml benzene was added a suspension of 3 1 m-mole Ph_3Bi in 50 ml benzene The solution was stirred during and after (for about 30 min) addition of the Ph_3Bi, and a light green precipitate, which began forming immediately, separ ated The supernatant benzene was decanted and fresh benzene added and the mixture sitted several min The pale green product was recovered by filtration, washing with benzene, and vacuum drying The compound turned dark brown with apparent decomposition at 190° and this residue then did not melt below 300° The equivalent conductance of a $4\ 4\times10^{-5}$ M solution of the compound in nitro methane was 136 mhos-cm^2, suggesting a 1 1 electrolyte

A new type of O-donor complex

16 *Tetrachloro(tropolono)uranium(V)tetratropolone* $UCl_4T\ 4HT$ The bidentate ligand tro polone



10 9 m-mole in 25 ml of benzene, was added to a solution containing ~2 5 m-mole UCl_5 TCAC in

benzene An immediate reaction ensued producing a finely divided, black precipitate The mixture was stirred overnight, the supernatant benzene decanted and fresh benzene added After the mixture had been stirred another 30 min the compound was filtered, washed with several small portions of benzene and vacuum dried Unlike any other U(V) compounds reported here, this compound is actually stable in air for more than a few min In fact, it can be exposed to air for several days before any color change occurs, in contrast to the other compounds which change color within seconds or minutes The black UCl_4T 4HT changes to a bright orange after being exposed to dry air for about 3 weeks However, it is quickly decomposed by most solvents It is slightly soluble in nitromethane but it decomposes within a few minutes even in this solvent Nevertheless, conductance measurements could be made in nitromethane and the data do not reveal any ions The differential thermal analysis curve for the compound showed a sharp endothermic peak at 207° The melting point obtained in a sealed tube was 125°

Compounds containing S-, Se , *and* Te-*donor ligands*

It is very likely that the compound of 2 mercaptopyridine, $UCl_5(2\ mcpy)_2$, already described (No 6 above) has the sulfur as well as the nitrogen coordinated to the uranium Below are described compounds obtained using Ph_2S_2 Ph_2Se_2 and Ph_2Te_2 as starting materials

17 *Tetrachloro(phenylsulfido)uranium(V)*, $[UCl_4(PhS)]_2$ The ligand, $C_6H_5SSC_6H_5$ dissolved in benzene was added in a 1 1 mole ratio, to a benzene solution of UCl_5 TCAC Immediately a gray precipitate formed and the mixture was stirred for about 1 hr and filtered It was washed with dry benzene several times and dried in vacuum The compound decomposes in $CHCl_3$, CH_2Cl_2, CH_3CN and CH_3NO_2, is insoluble in H_2O, goes slowly into dilute HNO_3 with decomposition

18 *Pentachloro(diphenyldiselenide)uranium(V)*, UCl_5 PhSeSePh This product was obtained using exactly the same procedure as described in 17, simply by substituting the analogous diselenide for disulfide as starting material The compound is insoluble in CH_2Cl_2 It dissolves in CH_3NO_2 but then the solution becomes turbid It dissolves in CH_3CN and $CHCl_3$

19 *Pentachloro(diphenylditelluride)uranium(V)*, UCl_5 PhTeTePh This product was obtained using exactly the same procedure as described in 17, simply by substituting the analogous ditelluride for disulfide as starting material The compound dissolves in $CHCl_3$, CH_2Cl_2, CH_3NO_2 and CH_3CN

Other ligands which led to impure and unpurifiable products after reactions with UCl_5 TCAC in benzene or in toluene are the following ammonia, 5-methyl 1,3,4 thiadiazole, piperidine dithiocarbamate thiosalicylic acid thiophene, tetracyanoethylene, triphenylantimony, diphenylsulfoxide, ethylenebis(diphenylarsine), methylenebis(diphenylarsine), diethylphenylphosphonite, and ethyldiphenylphosphonite

Analyses and physical measurements

Analytical analyses for uranium were done by reduction of the uranium(V) to uranium(IV) using a Jones reductor followed by titration to uranium(VI) with standard potassium dichromate solution Chlorine analyses were obtained from a commercial laboratory and/or measured in our laboratory either by Volhard titration or gravimetrically as silver chloride The nature of the compound dictated the method used Analyses for carbon, hydrogen and nitrogen were performed in our own laboratories by a staff member (Mr R Seab) and many were double checked by a commercial laboratory The latter also performed the analyses reported for P, As, S, Se, and Te

Equivalent conductances were obtained from measured resistances of 10^{-3}–10^{-5} M nitromethane solutions using a closed cell whose cell constant was determined using a standard potassium chloride solution

Magnetic susceptibility measurements were carried out at ambient temperature by the Guoy method Hydrated ferrous ammonium sulfate and mercury tetraisothiocyanatocobaltate(II) were used to calibrate the sample tubes All values were corrected for diamagnetism of the ligands

Electron spin resonance spectra were recorded on a JEOL-CO JES-3BX X-band spectrometer at ambient temperature The sealed sample tubes had an argon atmosphere

Vibrational spectra were recorded on a Beckman IR-10 or IR-7, with CsI optics used for the 200–600 cm^{-1} region Mineral oil mulls were pressed between NaCl plates or CsI plates depending upon the region being investigated The mulls were prepared in the dry box or an inert atmosphere glove bag and the edges of the plates covered with tape to protect the mull from air and moisture as much as possible

Electronic spectra were recorded in the 400–25,000 cm^{-1} region on a Cary 14R spectrophotometer, both at ambient temperature and at 77°K Mineral oil mulls of the sample were spread on filter paper and mounted on a brass plate in an argon atmosphere and then the plate was quickly immersed into an optical Dewar flask containing liquid nitrogen A mull on filter paper was placed in the reference beam Solution spectra for some of the compounds were obtained using matched 1,5, or 10 cm quartz cells

Mass spectra were run for a few of the compounds using a Varian M-66 instrument operated by a staff member, Mrs Cheryl White

RESULTS AND DISCUSSION

Some of the results, viz. colors, elemental analyses, decomposition temperatures, magnetic moments, average ESR determined g values and signal widths are collected in Table 1. None of the new compounds melt without decomposition although several are thermally stable to over 200°C. Many of the compounds are extremely sensitive to and decomposed by both air and moisture. Presumably the air oxidizes the uranium to the very stable UO_2^{2+} species, whereas moisture (alone) causes hydrolysis followed by disproportionation of the U(V) species to U(IV) and UO_2^{2+} species. We have verified these modes of decomposition at least qualitatively for several of the new compounds, but have not studied any reactions in detail. However, since there are no known complexes of U(VI) with ligands having phosphorus or arsenic or selenium or tellurium donor atoms, this may yet prove to be the route to such compounds and we hope to explore that possibility in the near future.

It is difficult to interpret the magnetic susceptibility data since we have no temperature-dependent data, and, therefore, no Weiss constants. The latter are often very high for U(V) compounds (see Ref. [1]) which renders magnetic moment values almost meaningless. Some of our values fall between the "spin-only" value of 1·73 B.M. and the value of 2·54 B.M. for a $5f^1$ ion in an essentially free condition (where then $\mu_{eff} = g[J(J+1)]^{1/2}$ and $g = \frac{6}{7}, J = \frac{5}{2}$, since $L = 3$ and $S = \frac{1}{2}$). Values in excess of 2·54 B.M. may result from any of several breakdowns in the foregoing formalized simplistic way of treating magnetism in a $5f^n$ system.

Perhaps the most striking physical data found for these new compounds are the ESR determined values for $<g>$ and the width of the ESR signals. There is but scant literature on electron spin resonance of pure uranium(V) compounds [6–9]. The only species apparently investigated thus far are either UX_6^- species [5–9] or $UX_5 \cdot L$, where L = TCAC or $SOCl_2$ or PCl_5 [5, 9], none of which contains ligands with heavily delocalized electronic systems such as the ones we report here. Thus, it becomes very significant that the $<g>$ values for the former complexes fall in the range 1·1–1·2 (when X = Cl) and the signal widths are extremely broad (~ 1200 Gauss), whereas for our new compounds the $<g>$ values are very close to the "free electron" value of 2·0023 and the signal widths are correspondingly small (2–40 Gauss). These narrow signals representing $<g>$ values close to the free electron value tempt us to postulate the existence of near free radical conditions within the complex molecules. Thus, the lone electron,

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9 E Stumpp, *Naturwissenschaften* **56**, 370 (1969)

formally presumed to be a strongly localized 5*f* electron, may actually be strongly delocalized into the pi-systems of the unsaturated organic molecules attached to the uranium(V). The ESR evidence thus suggests that the uranium electron finds a lower energy state on the organic ligand, making the latter essentially a free radical, which then may be (at least formally) considered to be attached to a uranium(VI) atom. Other evidence (such as that from both the i.r. and the optical spectra) suggests that some intermediate state may come closer to describing the true picture here. The NMR spectra of the complexes support, but do not prove, the delocalization picture since all ligand proton peaks are shifted so strongly as to be no longer observable.

I.R. spectra were obtained using the mineral oil mull technique for all of the compounds listed in Table 1 and for all of the free ligands themselves, from 4000–290 cm^{-1}. The spectra[10] confirm the presence of the organic ligands in each case and confirm also the *absence* of uranium(VI) as UO_2^{2+}. The latter ion may be revealed by a strong, moderately broad band in the 920–940 cm^{-1} region (ν_3) and a less intense (sometimes missing) band in the 830–860 cm^{-1} region (ν_1). Since the compound $UCl_5 \cdot Ph_3PO$ had already been reported and its i.r. spectrum measured[11] and since Ph_3P may be oxidized to Ph_3PO, it was important (even though great care was taken to exclude oxygen during our preparations) to establish that our complex with Ph_3P actually contained this molecule and not the phosphine oxide. Bagnall *et al.*[11] reported that the P=O band, found at 1192 cm^{-1} in the free ligand, is shifted to 973 cm^{-1} in the complexed ligand, whereas others[12] have reported shifts on complexation of P=O to other metal ions to the 1063–1093 cm^{-1} region. Our $UCl_5 \cdot Ph_3P$ does not exhibit any strong bands in either of these regions not attributable to the free Ph_3P. Mass spectral data support the conclusion reached from the i.r. data (*vide infra*). Similarly, the i.r. spectrum of UCl_5(EBDPP) rules out the possibility of this compound containing phosphine oxide. Furthermore, the absence of bands in the region of 2430 cm^{-1}, where P–H bands are usually observed[13], is good evidence that we are not dealing with phosphonium salts. On the other hand, we find a band at 265 cm^{-1} for $UCl_5 \cdot Ph_3P$ and at 272 cm^{-1} for UCl_5(EBDPP), each of which is reasonably assignable to the U–P vibration, which (because there were no U–P bonds known before this) has not been assigned previously.

Similarly, the i.r. spectrum of $[U_2Cl_9(Ph_3As)]Cl$ gives no evidence of an arsenic–oxygen bond. For example, the As=O band which occurs at 880 cm^{-1} in free Ph_3AsO has been reported[14] to be shifted about 40 cm^{-1} to lower frequencies upon complexation yet we find no band in this region for our complex. The U–As band is expected to be at lower frequencies than were experimentally accessible to us.

Uranium(V)–chlorine frequencies have been assigned for three UCl_6^- com-

10 Neither the spectra nor the hundreds of numbers representing bands will be given here, but these may be obtained for any given compound or for all of them from the authors Certain specific pertinent bands will be given in the text.

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13 P Gans and B C Smith, *J chem Soc* 4172 (1964)

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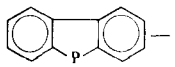
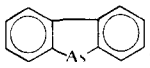
pounds and one UCl_8^{3-} compound between 303 and 310 cm^{-1}, at 285 cm^{-1} for $UCl_5 \cdot Ph_3PO$, and at 304 cm^{-1} for $UCl_5(C_8H_{17})_3PO$[15], and at 320 cm^{-1} in Pr_4NUCl_6[4]. We now assign as ν–Cl frequencies bands we find at 327, 315, and 310 cm^{-1} in [UCl_4dipy]Cl; at 325, 318, and 310 cm^{-1} in $UCl_5 \cdot Ph_3P$; at 330, 318, and 308 cm^{-1} in UCl_5(EBDPP); at 328, 317, and 305 cm^{-1} in [$U_2Cl_9(Ph_3As)$]Cl. Assignments of other bands in our complexes, such as U–O, U–N, U–S, etc. are not firmly based and will not be given here[16].

Mass spectral data was obtained for several of the new compounds when it was believed that this data would aid in the formulation of the complexes. For example, with the $UCl_5 \cdot Ph_3P$, no parent peak was found (which was true in all cases due to decomposition of the complexes prior to volatilization) but Ph_3P itself and fragments derived from it—such as $(Ph_2P)_2$, Ph_2P, PhP, Ph, and  were detected. Significantly no Ph_3PO or any of its potential oxygen-containing fragments were found. Likewise with [$U_2Cl_9(Ph_3As)$]Cl, the fragments clearly present were Ph_3As, Ph_2As, PhPh, PhAs, Ph, Ph_2AsCl, PhCl, PhCl, AsC_6H_4Cl, and  . Again, perhaps the most significant result is that no peaks appear for Ph_3AsO or any of its oxygen-containing fragments.

With the 8-hydroxyquinoline compound the most prominent peaks are due to the parent ligand itself (C_9H_7NO), to the parent minus $CO(C_8H_7N)$ and to C_7H_6 and C_7H_5. With the tropolone complex three strong peaks appear due to HT itself ($C_7H_5O_2H$), the parent minus $CO(C_6H_5OH)$ and a mass 78 fragment (C_6H_6) which we believe arises in the following manner. A coordinated tropolone molecule breaks away from the uranium atom leaving behind one oxygen ($C_7H_6O_2$–O=C_7H_6O) which then loses CO (as *tropone*, C_7H_6O, is known to do) giving the detected C_6H_6.

The electronic spectra of U(V) compounds have only been studied a few times[1, 2, 4] and then only in detail for the very regular (presumably O_h symmetry) species UX_6^- (X=F or Cl). Rather firm assignments have been made, for example, of the four groups of bands found in the spectrum of UCl_6^- (in $SOCl_2$)[4] to the four predicted electronic transitions, $\Gamma_7 \rightarrow (\Gamma_8, \Gamma_7', \Gamma_8', \Gamma_6)$, which arise from a $5f^1$ ion in a O_h ligand field. The ground term $^2F_{5/2}$ splits in this field into a lower-lying (Kramers) doublet, Γ_7, and an upper quartet Γ_8. The excited term, $^2F_{7/2}$, splits into the three terms: Γ_7' (doublet), Γ_8' (quartet) and Γ_6 (doublet).

All of our compounds, whose electronic spectra[10] were run in mulls at 77°K exhibit more complex spectra than UCl_6^-, understandably, and we are not yet prepared to offer an interpretation of these spectra. However, it does seem clear to us from the spectra that we are indeed dealing with U(V) complexes (and not U(IV)) but that the attachment of unsaturated ligand systems to the U(V) has had a definite effect upon what might otherwise be transitions primarily confined to the electronic levels of a $5f^1$ system. For one compound at least, UCl_5(EBDPP), we were able to obtain both a solid state (mull at 77°K) spectrum

15. K. W. Bagnall, D. Brown and J. G. H. DuPreez, *J. chem. Soc.* 2603 (1964).
16. We have nevertheless made such assignments on a tentative basis and would be happy to communicate the data and assignments to those interested.

and a solution (in CH_3CN at R.T.) spectrum. The essential identity of most strong band positions (with some minor shifts) suggests that at least for this complex there is essentially no change in the main absorbing species upon dissolution. Other compounds were either not soluble enough for spectral purposes or were rapidly decomposed by the solvent.

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PREPARATION AND CHARACTERIZATION OF LITHIUM- AND TETRAALKYLAMMONIUM TETRABUTYLALUMINATES

T D WESTMORELAND, JR NASEER AHMAD* AND M C DAY**
Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803 (U S A)
(Received June 15th 1970)

SUMMARY

Lithium tetra-n-butylaluminate ($LiAlBu_4$) has been prepared by reacting n-hexane solutions of n-butyllithium and tri-n-butylaluminum The tetraalkylammonium tetra-n-butylaluminates (R_4NAlBu_4, R = Me, Et, n-Pr, n-Bu) have been prepared in benzene by the addition of sodium tetra-n-butylaluminate ($NaAlBu_4$) to solutions of R_4NBr The significance of the syntheses of these salts for the study of ion–ion and ion–solvent interactions has been discussed

The tetra-n-butylaluminate salts have been characterized by aluminum analyses, NMR spectroscopy, solubility data, melting points, and conductance data The similarity between the physical and chemical properties of the R_4NAlBu_4 salts and $NaAlBu_4$, which has been extensively used for ion–solvent studies, indicates the potential value of these quaternary ammonium salts in analogous investigations

INTRODUCTION

The unique ability of sodium tetra-n-butylaluminate ($NaAlBu_4$) to dissolve in solvents of low dielectric constant, including saturated hydrocarbons, has facilitated the study of specific ion-solvent interactions without interference from the bulk solvent[1] A number of investigations utilizing this property of $NaAlBu_4$ have now been made on the specific complexation of the sodium ion by basic solvents[1-7] Ideally, one would like to extend studies of this type to include the effect of cation size, but this would require a series of salts having a common anion with significant solubility in noncoordinating solvents

Sodium tetra-n-butylaluminate has the distinct advantage of appreciable solubility in a variety of solvents, including those that can be considered essentially inert towards complexation With the intent of conducting a study of the effects of cation size on both ion–solvent and ion–ion interactions, we have attempted to prepare a series of tetra-n-butylaluminate salts with the anticipation of solubility and ionic characteristics similar to those of the sodium salt

We feel that the simple presentation of physical data and analyses is often in-

* On study leave from Aligarh Muslim University, Aligarh, India
** To whom correspondence should be addressed

adequate in the identification of certain chemical compounds, especially those which have been prepared for specific purposes. We have thus attempted to characterize the compounds which we have synthesized by presenting a cursory examination of experimental results, utilizing techniques which have been used in this laboratory for the study of $NaAlBu_4$.

The lithium salt, unfortunately, appears to be insoluble in non-polar solvents at ambient temperatures, and the potassium, cesium, and ammonium salts have never been successfully prepared in this laboratory. The preparation of the quaternary ammonium salts (R_4NAlBu_4), however, has been effected, and they are all appreciably soluble in benzene at room temperature. We wish to report here the preparative procedure for these salts, as well as that of lithium tetra-n-butylaluminate ($LiAlBu_4$), and to present their characterization.

RESULTS AND DISCUSSION

Proton magnetic resonance

The NMR spectra of aqueous solutions of the R_4NBr salts were recorded by a 60 MHz spectrometer, and the proton signals were analyzed. The proton resonance spectrum of $NaAlBu_4$ has previously been studied extensively in this laboratory[1], and a portion of the spectrum has been published by Wuepper and Popov[6]. The spectra which we recorded for the 0.1 *M* benzene solutions of the R_4NAlBu_4 salts were almost composite pictures of the spectra of the starting materials, $NaAlBu_4$ and R_4NBr. A 100 MHz spectrometer was used to obtain spectra of 250 Hz width to study the areas of the spectra in which overlap of the proton signals from the alkyl groups on the nitrogen and the aluminum occurs. Integration of the peaks gave no quantitative results because of the overlapping of the signals, but the constancy of the relative peak heights of the various alkyl groups in many different samples eliminates the possibility of a simple admixture of the two starting materials in the benzene solutions. Corroborative data confirm this.

The spectrum of $LiAlBu_4$ was taken in tetrahydrofuran (THF) because of this compound's limited solubility in benzene. The proton signals were very nearly identical to those of $NaAlBu_4$ in THF. No signals from n-butyllithium or tri-n-butylaluminum were detected.

Melting points and aluminum analyses

Table 1 lists the melting points which were obtained for the lithium and the quaternary ammonium salts. The melting points of $NaAlEt_4$ and $NaAlBu_4$ are included for purposes of comparison. It should be noted that the melting point for $NaAlBu_4$ is slightly higher than that reported in the literature[1,6]. The close agreement between the experimental and the theoretical percentages of the aluminum analysis and the refinement of the preparative procedure for the salt lead us to believe that our value is more nearly correct. The inclusion of the melting point of $NaAlBu_4$ is intended to show the proximity of its melting point to the melting points of the R_4NAlBu_4 salts. The much higher melting point of $NaAlEt_4$[8,9], as compared to that of $NaAlBu_4$, indicates that the forces of attraction in the crystalline state are more alike among the five tetra-n-butylaluminates than for the $NaAlBu_4$ and its tetraethyl analog. Moreover, the tetramethyl- and tetraethylammonium tetraethylaluminates, as re-

TABLE 1

MELTING POINTS AND ALUMINUM ANALYSES OF TETRAETHYL- AND TETRA-n-BUTYLALUMINATES

Salt	M p (°C)	% Al	
		Calcd	Found
$NaAlEt_4$	ca 125[8,9]	16 23	16 11, 16 18
$NaAlBu_4$	67–69	9 69	9 67
$LiAlBu_4$	181–183	10 3	10 1
Me_4NAlBu_4	68–70	8 19	8 11
Et_4NAlBu_4	74–76	6 99	7 10
Pr_4NAlBu_4	52 54	6 11	6 02
Bu_4NAlBu_4	49 50	5 42	5 41
Me_4NAlEt_4	162 165[10]	12 5	[a]
Et_4NAlEt_4	185–189[10]	9 86	[a]

[a] Analyses not given

ported by Zakharkin *et al* [10], show much higher melting points than any of the R_4NAlBu_4 salts We are led to suspect that the presence of the tetra-n-butylaluminate anion in the crystal structure is at least partially responsible for the lower melting points of these salts and perhaps for their greater solubilities in solvents of low dielectric constant Until definitive X-ray work is done on these salts, however, it would be premature to attempt to draw conclusions

The aluminum analyses are also included in Table 1 The analyses were difficult to obtain because of the air-sensitivity of these compounds and the difficulty of removing the solvents, however, the results show good agreement with the theoretical values

Carbon and hydrogen analyses were not made because of their unreliability for these air-sensitive compounds

Solubility

An attempt was made to carry out a solubility study on these salts in solvents of interest with the intent of compiling a solubility chart for the compounds However, the lithium salt is not soluble in saturated hydrocarbons and shows appreciable solubility in benzene only at elevated temperatures The R_4NAlBu_4 salts form two phases in the presence of saturated hydrocarbons and dissolve in benzene so readily that only an estimate of their solubility in benzene could be made The R_4NAlBu_4 salts are at least as soluble in benzene as $NaAlBu_4$ is in cyclohexane (ca 3 *M*)[1], however, at higher concentrations in benzene large globular particles can be seen on close inspection The extent of this effect is dependent on the salt and the temperature Further addition of benzene gives a clear solution The quaternary ammonium salts are very soluble in THF but, surprisingly, must be heated in order to prepare even 0 1 *M* solutions

Conductance

Table 2 lists the equivalent conductances of the salts in 0 1 *M* and 0 01 *M* solutions of benzene and THF The cursory examination of the conductances of the salts is intended primarily to show the extent of their ionicity Conductance studies

TABLE 2

SUMMARY OF EQUIVALENT CONDUCTANCES OF SOLUTIONS OF BENZENE AND TETRAHYDROFURAN

Salt	$\Lambda^a \times 10^2$ in benzene (cm^2 equiv^{-1} ohm^{-1})		$\Lambda^a \times 10^2$ in THF (cm^2 equiv^{-1} ohm^{-1})	
	0.1 *M*	0.01 *M*	0.1 *M*	0.01 *M*
$NaAlEt_4$	Insol	Insol	2400	1260
$NaAlBu_4$	1.8	0	2290	980
$LiAlBu_4$	Insol	0	630	1560
Me_4NAlBu_4	5.3	0.8	0	1550
Et_4NAlBu_4	0	1.1	0	1650
Pr_4NAlBu_4	0	1.8	0	1560
Bu_4NAlBu_4	32	1.1	430	500

[a] Equivalent conductance

of $NaAlBu_4$ in cyclohexane and THF indicate that the sodium salt exists as some sort of ionic species in these solvents. We had hoped simply to show the similarity between the conductances of the R_4NAlBu_4 salts and $NaAlBu_4$ in order to further characterize the salts and to illustrate the potential usefulness of the compounds as ionic species which are soluble in solvents of low dielectric constant. However, it is obvious upon inspection of the conductance data that not only is the ionicity of the quaternary ammonium salts clearly demonstrated, but some rather interesting behavior is shown.

Inspection of Table 2 reveals the relative magnitude of the equivalent conductances of the sodium and the lithium salts. In THF, the differences in equivalent conductances for these salts may be rationalized in terms of apparent differences in ion mobilities, but, obviously, the possibility of ion pairs and higher aggregates must also be considered. It is particularly interesting to note the increase in equivalent conductance with an increase in salt concentration for the sodium salts in THF; whereas, the reverse is observed for the lithium and the R_4NAlBu_4 salts in this solvent.

The equivalent conductances of the R_4NAlBu_4 salts cannot be readily rationalized. In terms of previous conductance studies on similar salts, we might attribute the low equivalent conductances to large degrees of association[11-16]. Table 2 shows that the quaternary ammonium salts in benzene have essentially the same conductances at the lower concentrations. It is apparent that the ion size plays an extremely important role in these sytems; a role that is now under study in this laboratory.

Reactivity

The R_4NAlBu_4 salts are unstable in the presence of air, water, oxygen, and alcohols, as has been observed with the corresponding sodium salt; however, they appear to be much less reactive in these systems than $NaAlBu_4$. $LiAlBu_4$ is more reactive than $NaAlBu_4$. All of the compounds appear to be quite stable in the hydrocarbons and ethers we have used in our investigations.

EXPERIMENTAL

Conductance

Conductance cells of standard design with shiny platinum electrodes were

used for all of the conductance measurements. The cells were fitted with outer ground-glass caps in order to prevent contamination of the solutions by the joint lubricant. The cell constants were determined by the use of potassium chloride solutions accordding to method of Lind *et al.*[17].

Conductance measurements were made by a Leeds and Northrup Model 4666 Jones Modified Conductance Bridge or by a RC-16 Conductance Bridge manufactured by Industrial Instruments, Inc. A Hewlett-Packard Model 200 D audio oscillator and a General Radio Company Type 1232 A tuned amplifier and null detector were used in conjunction with the Leeds and Northrup instrument. The oscillator was operated at 3000 Hz and had an output to the bridge of 0.5 V. The maximum resistance measurable on the RC-16 Conductance Bridge is 2.5 MΩ; that on the Jones Bridge is 60 kΩ. Measured resistances were taken with the Jones Bridge whenever possible. The temperature of the solutions were maintained at $30 \pm 1°$.

The conductance cells were thoroughly washed in acetone, ethanol, water, 20% HCl solution, 50% H_2SO_4 solution, and conductivity water before they were dried in an oven at 120° for several hours. The cells were taken directly from the oven and placed under vacuum in the port to the nitrogen-atmosphere dry box while they cooled. The conductance cells, as well as all other equipment and chemicals taken into the dry box, were kept in the port while the nitrogen atmosphere in the port was recirculated through a series of columns and traps to remove any traces of oxygen and moisture[2].

Conductances were not observed for the purified solvents; consequently, no corrections for solvent conductance were necessary. Conductance values for the solutions did not vary significantly over a 24 h period.

Proton magnetic resonance

The proton magnetic resonance spectra were taken for all compounds on the Varian Associates A-60A and HA-100 spectrometers at ~37°. NMR tubes were filled in the dry box and sealed with high pressure caps. Samples were run within approximately two hours of the time the tubes were removed from the dry box.

Solvents and reagents

All solvents were purchased as reagent grade chemicals. They were allowed to stand over CaH_2 until no further reaction was visible, refluxed over the CaH_2 for a minimum of 8 h, and distilled under an atmosphere of dry nitrogen gas. A portion of each solvent was poured over small amounts of the sodium and lithium salts of tetra-n-butylaluminate to test for traces of water and oxygen before the solvent was used. The THF was used within a period of 48 h from the time it was taken into the dry box.

The preparation and purification of $NaAlBu_4$ and $NaAlEt_4$ have been discussed in previous publications[1,8,9]. The R_4NBr salts were purchased as highest purity salts (Eastman Organic and J. T. Baker). They were subjected to a vacuum for several hours before use. Recrystallization was not deemed necessary for the use of the salts in the preparatory procedures.

The n-butyllithium (Alfa Inorganics) was used as a 22% hexane solution, and was filtered through glass wool in the dry box before use.

The tri-n-butylaluminum (Texas Alkyls) was used as a 95.9% pure reagent (highest purity) without further purification.

Preparation of $LiAlBu_4$

The procedure for the preparation of $LiAlBu_4$ is similar to that of Hurd's[18] preparation of $LiAlMe_4$. An equimolar ratio of tri-n-butylaluminum in hexane was added to n-butyllithium (22% hexane solution) in an inert atmosphere. The white crystals which formed immediately upon the mixing of the two solutions were filtered and washed with hexane four times. Recrystallization was effected in hot toluene. Washing with hexane, followed by the application of a vacuum to the crystals as they were rotated in a flask connected to a high vacuum rotating evaporator, gave fluffy white crystals.

Preparation of the R_4NAlBu_4 salts

All of the R_4NAlBu_4 salts were prepared by the same general procedure of refluxing a given quantity of the appropriate R_4NBr salt in benzene under a nitrogen atmosphere for 24–48 h in order to attain maximum solubility of the salt before adding a benzene solution of $NaAlBu_4$ dropwise to the refluxing mixture. A slight molar excess of the R_4NBr was used. The admixture was refluxed further for approximately 24 h. The NaBr and excess R_4NBr were removed by filtration in the dry box. The resultant solution was subjected to a vacuum until a viscous solution was obtained; whereupon, the solution was filtered again. The filtrate was washed with hexane several times to extract any excess $NaAlBu_4$ and then placed under vacuum in a high vacuum rotating evaporator until a thick slurry was obtained. Filtration of the slurry gave white crystals. After being washed with hexane, the crystals were heated to $\sim 100^\circ$ while being subjected to a vacuum to remove the last fraction of benzene and hexane.

Recrystallization was never adequately effected because of the large degree of solubility of the salts in benzene and their unusual property of forming two phases in the presence of hexane. Hence, the above procedure was repeated until a two degree (or less) melting point range was obtained for each salt. Both THF and diethyl ether were used as the carrying solvent in the initial studies, but the difficulty of the complete removal of the ethers caused us to rely on benzene.

The possibility of synthesizing R_4NAlR_4 compounds was reported by Lehmkuhl[19], although no preparative procedure was offered.

Aluminum analysis

The aluminum analyses were carried out on these salts according to a slight modification of the procedure outlined by Kolthoff and Sandell[20]. An average value of two or more analyses was reported for each salt.

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Congo Red Complexes with Some Rare-Earth Salts.

S. M. F. Rahman, Naseer Ahmad, and Jamil Ahmad

Congo red forms brick red coloured water insoluble complexes with the chlorides of lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium and dysprosium in aqueous solution at feebly acidic *p*H of 6·5. They have been studied in water medium at *p*H 6·5 conductometrically and their complexes have been isolated and analysed.

EXPERIMENTAL

Congo red (BDH grade) was dissolved in water to make 0·01*M* solution. The rare-earth salts solutions were made as mentioned in earlier works[1]. The *p*H of water used all along the experiments were adjusted to 6·5 by the addition of requisite quantity of dilute hydrochloric acid.

Philips conductivity Bridge Model (PR 9500) was used for both direct and reverse conductometric titrations. The concentration of the solutions used were of the order of $0{\cdot}5-1\times10^{-3}M$ to $0{\cdot}5-1\times10^{-2}M$.

0·01*M* solution of congo red and a rare earth salt (La, Ce, Pr, Nd, Sm, Gd and Dy) in water was mixed in equal proportion and the precipitate thus obtained was separated by centrifugation, washed with water and alcohol, and dried in vacuum over quick-lime at room temp. of 30°. Microanalysis for the determination of carbon, sulphur, nitrogen and hydrogen was done by the courtesy of Micro Analytical Service, Melbourne, Australia. For the analysis of the metal the complex was fused with fusion mixture in a platinum crucible and the fused mass was dissolved in dilute hydrochloric acid and the rare earth estimated[2].

For the estimation of chloride the fused mass as above was dissolved in dilute nitric acid and the chloride was estimated as silverchloride[3]. The results of analysis is given in Table 1.

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TABLE 1

Congo red complexes with rare-earth salts

	metal	C	N	H	S	Cl
1. *Lanthanum Complex* :						
Value calculated for $La(H_{22}C_{32}N_6S_2O_6)Cl$	16.85%	46.57%	10.18%	2.66%	7.76%	4.30%
Value observed	16.78%	46.51%	10.08%	2.67%	7.74%	4.28%
2. *Cerium Complex* :						
Value calculated for $Ce(H_{22}C_{32}N_6S_2O_6)Cl$	16.95%	46.51%	10.17%	2.66%	7.75%	4.29%
Value observed	16.86%	46.50%	10.16%	2.67%	7.68%	4.26%
3. *Praseodymium Complex* :						
Value calculated for $Pr(H_{22}C_{32}N_6S_2O_6)Cl$	17.08%	46.46%	10.16%	2.66%	7.74%	4.29%
Value observed	16.98%	46.45%	10.14%	2.68%	7.68%	4.28%
4. *Neodymium Complex* :						
Value calculated for $Nd(H_{22}C_{32}N_6S_2O_6)Cl$	17.35%	46.29%	10.12%	2.65%	7.71%	4.28%
Value observed	17.28%	46.28%	10.08%	2.66%	7.69%	4.28%
5. *Samarium Complex* :						
Value calculated for $Sm(H_{22}C_{32}N_6S_2O_6)Cl$	17.95%	45.96%	10.00%	2.63%	7.66%	4.25%
Value observed	17.97%	46.93%	9.98%	2.65%	7.69%	4.24%
6. *Gadolinium Complex* :						
Value calculated for $Gd(H_{22}C_{32}N_6S_2O_6)Cl$	18.63%	45.57%	9.97%	2.61%	7.59%	4.21%
Value observed	18.62%	46.51%	9.96%	2.63%	7.58%	4.21%
7. *Dysprosium Complex* :						
Value calculated for $Dy(H_{22}C_{32}N_6S_2O_6)Cl$	19.10%	45.28%	9.90%	2.59%	7.54%	4.18%
Value observed	19.05%	45.24%	9.88%	2.61%	7.54%	4.17%

RESULTS AND DISCUSSION

Congo red forms 1 : 1 complexes with the chlorides of La, Ce, Pr, Nd, Sm, Gd, and Dy which is substantiated by the result of both direct and reverse conductometric titrations.

The formation of 1 : 1 complexes may be explained on the basis of the replacement of two sodium atoms of the disodium salt of the ligand (Congo red) by a trivalent rare-earth ion to give a closed packed structure. The highly soluble nature of the ligand and the insoluble nature of the complex in water medium further support the above view. On the basis of the above results the formula of the complexes may be suggested as $(C_{32}H_{22}N_6S_2O_6)MCl$ where M stands for La, Ce, Pr, Nd, Sm, Gd, and Dy.

Department of Chemistry,
Aligarh Muslim University,
Aligarh.

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Titan Yellow Complexes of some Rare-Earth Salts

S. M. Fazlur Rahman, Naseer Ahmad and Jamil Ahmad

Chlorides of Lanthanum, Cerium, Praseodymium, Neodymium, Samarium, Gadolinium, and Dysprosium react with titan-yellow to form yellowish brown coloured water insoluble complexes. They have been studied, in water at feebly acidic medium of 6·5-*p*H, by direct and reverse conductometric titrations, isolated and analysed.

EXPERIMENTAL

The oxides of La, Ce, Pr, Nd, Sm, Gd, and Dy (Chemistry Division, Bhabha Research Centre, India Product) were converted into chlorides by evaporation with hydrochloric acid. (A.R. BDH grade). Titan yellow (BDH grade) was dissolved in water to make 0·01 *M* solution. The rare-earth salts solutions were prepared as mentioned in earlier works[1]. The *p*H of water used was adjusted by the addition of requisite quantity of dil.HCl.

Philips Conductivity-Bridge model (PR 9500) was employed for conductometric titrations. Both direct and reverse titrations were carried out in all these cases. The concentrations of the solutions used were of the order of $0{\cdot}5-1\times10M^{-3}$ to $0{\cdot}5-1\times10\ M^{-2}$.

TABLE 1

Titan yellow complexes with Rare-earth Salts

Complex	Results of Analysis					
	Metal%	C%	H%	N%	S%	Cl%
1. Lanthanum	16.84	40.76	2.31	8.46	15.07	4.28
$La(H_{19}C_{28}S_4N_5O_6)Cl$,%	(16.87)	(40.80)	(2.30)	(8.50)	(15.54)	(4.32)
2. Cerium	16.94	40.71	2.31	8.45	15.43	4.28
$Ce(H_{19}C_{28}S_4N_5O_6)Cl$ %	(16.98)	(40.75)	(2.30)	(8.49)	(15.52)	(4.30)
3. Praseodymium	17.10	40.61	2.30	8.43	15.46	4.28
$Pr(H_{19}C_{28}S_4N_5O_6)Cl$, %	(17.08)	(40.70)	(2.30)	(8.48)	(15.50)	(4.30)
4. Neodymium	17.29	40.48	2.30	8.41	15.41	4.27
$Nd(H_{19}C_{28}S_4N_5O_6)Cl$, %	(17.38)	(40.55)	(2.29)	(8.44)	(15.45)	(4.28
5. Samarium	17.94	40.13	2.28	8.37	15.31	4.25
$Sm(H_{19}C_{28}S_4N_5O_6)Cl$, %	(17.97)	(40.26)	(2.27)	(8.38)	(15.34)	(4.25
6. Gadolinium	18.64	39.86	2.25	8.30	15.18	4.20
$Gd(H_{19}C_{28}S_4N_5O_6)Cl$, %	(18.65)	(39.92)	(2.25)	(8.31)	(15.21)	(4.21
7. Dysprosium	19.10	39.61	2.23	8.25	15.03	4.18
$Dy(H_{19}C_{28}S_4N_5O_6)Cl$, %	(19.13)	(39.69)	(2.26)	(8.26)	(15.12)	(4.19

Figures in the parentheses indicate calculated values.

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0·01 *M* solutions of titan yellow and a rare-earth salt (La, Ce, Pr, Nd, Sm, Gd, and Dy) in water were mixed in equal proportion and the precipitate thus obtained was separated by centrifugation, washed with water and alcohol, dried over quicklime in vacuum and analysed. The analytical data on carbon, hydrogen, nitrogen and sulphur were obtained through the courtesy of Australian Micro Analytical Service, Melhourne, Australia. For the analysis of the metal the complex was fused with fusion mixture in a platinum crucible, the melt was dissolved in dilute hydrochloric acid and the rare-earth metal estimated[2]. For the estimation of chloride the melt as above was dissolved in dilute nitric acid and the chloride was estimated as silver chloride. The analytical results are given in Table 1.

RESULTS AND DISCUSSION

Titan yellow form 1 : 1 complexes with the chlorides of La, Ce, Pr, Nd, Sm, Gd, Dy which is substantiated by the result of both direct and reverse conductometric titrations. On the basis of the analytical results the formula may be suggested as $(C_{28}H_{19}S_4N_5O_6)$ MCl where M stands for the rare earths.

Department of Chemistry,
Aligarh Muslim University,
Aligarh.

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Complexes of chromium(II) chloride with some sulphur-containing amino acids

The interaction of transition metal ions with amino acids covers a vast area of research because of its biological importance, and the coordinating ability of amino and carboxylic groups[1-3] However, very few papers deal with the interaction of amino acids with transition metals having abnormal oxidation states Recently a systematic study on this aspect of the problem was undertaken by the authors and the complexes of Cr^{2+}, UO_2^{2+}, VO^{2+} and Ti^{3+} with non-sulphur containing amino acids were studied[4,5] The present communication deals with the composition of various sulphur-containing amino acid complexes, based upon pH-metric and potentiometric measurements

Experimental

The amino acids, DL-methionine, taurine and cysteine (B D H Biologically pure products) were used and 0 01 *M* solutions were prepared in doubly distilled air-free water Chromous chloride was prepared by the method of Bathis and Bailer[6] The aqueous solution of chromous chloride was prepared as described previously, and stored in an air-tight storage vessel under an atmosphere of oxygen-free nitrogen (pH 3 5) The solution was standardized potentiometrically by titration with standard copper sulphate Carbonate-free KOH was used to prepare an aqueous solution of KOH and the solution was kept in a Pyrex bottle fitted with a guard tube containing KOH for protection against atmospheric carbon dioxide The solution was standard-

ized by titrating with standard oxalic acid and checked periodically before carrying out the pH-metric titrations.

The potentiometric titrations were carried out with a Tinsley potentiometer having a lamp and scale arrangement and employing platinum and calomel electrodes. The pH-metric titrations were performed with a direct reading EIL pH-meter model 23A (England). All the titrations were carried out in a specially designed cell described previously. The concentration of chromous chloride was checked before studying each system. All investigations were carried out at 25°C.

Results and discussion

Chromous chloride forms 1 : 1 complexes with DL-methionine, taurine and cysteine as determined from potentiometric curves (Fig. 1). The titrations were carried out using various concentrations of chromous chloride in the cell and equimolar solution of amino acids. The information regarding complex formation was obtained by noting the shifts in the pH-titration curves.

For each amino acid three sets of pH-metric titrations using 0.1 *N* KOH as a titrant were carried out in the order: (a) amino acid 0.01 *M*, (b) chromous chloride 0.005 *M* and (c) a mixture of chromous chloride and amino acid having a total concentration of 0.005 *M* and 0.01 *M*, respectively, (Fig. 2).

The values of the logarithm of the formation constant, log K_s at $\bar{n}=1$ (where $\bar{n}$ is the average number of molecules of amino acid bound by one atom of the metal) for the amino acids were calculated from the values of $-\log [Sc]$ obtained by the plot of $\bar{n}$ *vs.* $-\log [Sc]$, where $[Sc]$ is the concentration of free amino acid (Fig. 3). By applying the relation $\log K_s = -2 \log [Sc]$, values of the formation constants for all three amino acids were evaluated[7]. The values obtained graphically and by calculation

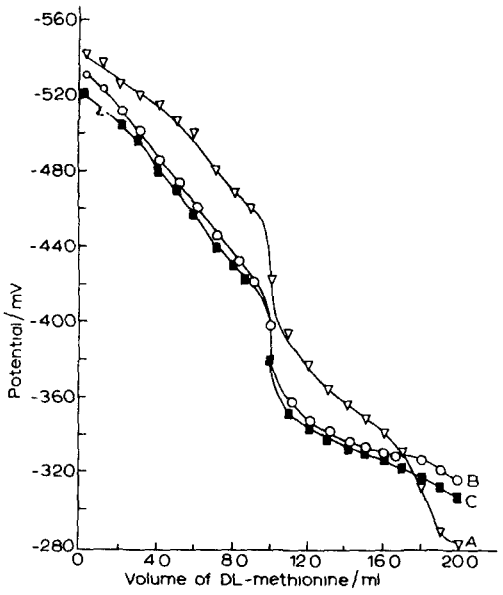
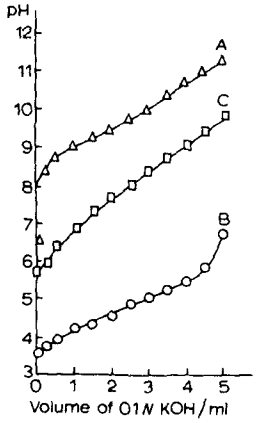


Fig 1 Potentiometric titrations (A) 10 ml 0.666×10^{-1} *M* $CrCl_2$ (in cell) *vs* 0.666×10^{-1} *M* DL-methionine (from burette), (B) 10 ml 0.50×10^{-1} *M* $CrCl_2$ (in cell) *vs* 0.50×10^{-1} *M* DL-methionine (from burette), (C) 10 ml 0.44×10^{-1} *M* $CrCl_2$ (in cell) *vs* 0.44×10^{-1} *M* DL-methionine (from burette)



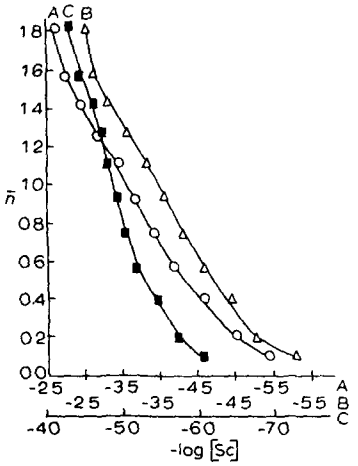


Fig 2 pH-metric titrations (A) 50 ml 0.01 *M* DL-methionine (in cell), (B) 50 ml 0.005 *M* $CrCl_2$ (in cell), (C) 25 ml 0.02 *M* DL-methionine + 25 ml of 0.01 *M* $CrCl_2$ (in cell).

Fig 3 Formation curves (A) DL-methionine–chromium(II) complex, (B) taurine–chromium(II) complex, (C) cysteine–chromium(II) complex

are given in Table 1.

The values of overall stability constants obtained from the formation curves are in good agreement with those calculated. The values of log K_s given in Table 1

TABLE 1

		log (K_s/mol^2 l^{-2})	
		Graphically	*Calcd*
1	Cysteine–chromium(II) chloride complex	9.80	9.77
2	DL-Methionine–chromium(II) chloride complex	7.32	7.30
3	Taurine–chromium(II) chloride complex	7.02	7.06

give an indication of the possible correlation between the nature of the amino acids and overall stability constants. The value of log K_s decreases as the distance between amino and carboxylic group increases (between NH_2 and $-SO_2OH$ in the case of taurine). The present studies do not clarify the part played by sulphur atoms.

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Department of Chemistry,
Aligarh Muslim University,
Aligarh U.P. (India)

Omar Farooq
A. U. Malik
Naseer Ahmad*

* Chemistry Department, Louisiana State University, Baton Rouge, La 70803, U.S.A.

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CONTRIBUTION FROM COATES CHEMICAL LABORATORIES,
LOUISIANA STATE UNIVERSITY, BATON ROUGE, LOUISIANA 70803

Preparation and Properties of Lanthanide Chelate Complexes

BY J. SELBIN,* N AHMAD, AND N BHACCA

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Compounds of five types have been synthesized $M(dpm)_3$ [M = Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu], $M(dpm)_3py$ [M = same 12 metals], $M(dpm)_3dipy$ [M = same first 11 metals, not Lu], $M(dpm)_3phen$ [M = same first 11 metals, not Lu], and $Ce(dpm)_4$ [where dpm = dipivaloylmethane, py = pyridine, dipy = α,α'-dipyridyl, phen = 1,10-phenanthroline] They have been characterized by their thermal (melting point, dta, tga), spectral (ir, visible, uv), and magnetic (susceptibility, Weiss constant) properties and are under investigation as proton nmr shift reagents

Introduction

The recently reported[1] discovery that the pyridine adduct of tris(dipivaloylmethanato)europium(III), $Eu(dpm)_3(py)_2$, could be used as a proton nmr shift reagent for cholesterol prompted us to begin the preparation of a series of analogous lanthanide complexes with the same bulky bidentate β-keto enolate ligand with all of the available lanthanide ions We wanted to explore more fully the potential of the various $4f^n$ systems as shift reagents for a variety of organic molecules and to see if we could determine and understand the specific characteristics which produce the best shift reagents More recent reports have established that (1) $Eu(dpm)_3$ itself (*i.e.*, without the pyridine molecules appended) is even better than the dipyridine adduct,[2] (2) the analogous praseodymium compound, $Pr(dpm)_3$, induces proton nmr shifts[3] of the opposite sign of those reported for $Eu(dpm)_3$ and also much larger than those reported for $Eu(dpm)_3$, (3) Eu(III), Gd(III), and Ho(III) cations will serve as nmr structural probes in several biological systems,[4] (4) when $Eu(dpm)_3$ serves as the shift reagent for adamantan-1- and -2-ol, the mechanism of deshielding involves interaction *both* through space (pseudocontact shift) and through bonds (contact shift),[5] and (5) $Eu(dpm)_3$ may be used as a shift reagent for a steroid and a triterpene [6]

We have now prepared 47 compounds of the types $M(dpm)_3$ (M = Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), $M(dpm)_3py$ (M = same 12 metals), M-

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TABLE I
COMPOUNDS PREPARED IN THIS STUDY AND SOME CHARACTERIZING DATA

Compd	Color	Analysis C Calcd	C Found	H Calcd	H Found	N Calcd	N Found	Mp,[a] °C	Magnetic moment[b]	Weiss constant
Ce(dpm)$_4$	Red	60.52	60.49	8.77	8.64	...	...	276	Diamag	
Pr(dpm)$_3$	Green	57.38	56.82	8.32	8.42	...	...	222–224	3.6, 3.7	
Pt(dpm)$_3$py	Green	59.29	59.74	8.12	8.22	1.82	1.75	...	...	
Pr(dpm)$_3$dipy	Green	60.98	60.28	7.74	7.77	3.31	3.14	191–193	3.6	
Pr(dpm)$_3$phen	Green	62.06	61.66	7.52	7.60	3.22	3.01	221–222	3.6	
Nd(dpm)$_3$	Violet	57.11	56.27	8.28	8.25	...	...	218–219	3.5, 3.7	
Nd(dpm)$_3$py	Violet	59.03	57.49	7.95	8.04	1.81	1.73	...	...	
Nd(dpm)$_3$dipy	Violet	60.74	59.25	7.70	7.67	3.29	3.14	189	3.7	
Nd(dpm)$_3$phen	Violet	61.82	61.44	7.49	7.59	3.20	3.18	222	3.7	
Sm(dpm)$_3$	White	56.61	56.47	8.21	8.46	...	...	200–201	2.1, 2.0	
Sm(dpm)$_3$py	White	58.57	58.02	8.02	8.14	1.80	1.64	133–135	2.4	
Sm(dpm)$_3$dipy	White	60.31	60.58	7.65	7.53	3.27	3.19	189–191	2.4	
Sm(dpm)$_3$phen	White	61.39	61.62	7.44	7.64	3.18	3.07	225–226	2.2	
Eu(dpm)$_3$	Yellow	56.48	56.58	8.19	8.41	...	...	190–191	3.6, 3.4	
Eu(dpm)$_3$py	White	58.45	58.66	8.00	8.17	1.79	1.76	135–138	3.7	
Eu(dpm)$_3$dipy	White	60.19	59.74	7.64	7.26	3.26	3.13	190–191	3.6	
Eu(dpm)$_3$phen	Light yellow	61.28	61.83	7.43	7.68	3.18	3.02	217–219	3.6	
Gd(dpm)$_3$	White	56.06	56.40	8.13	8.39	...	...	183–184	7.8, 7.6	175
Gd(dpm)$_3$py	White	58.06	56.85	7.95	7.95	1.78	1.65	134–135	7.8	
Gd(dpm)$_3$dipy	White	59.83	60.20	7.59	7.82	3.24	3.18	192–193	7.9	
Gd(dpm)$_3$phen	White	60.91	60.16	7.38	7.57	3.16	3.02	225–228	8.0	
Tb(dpm)$_3$	White	55.93	55.99	8.11	8.34	...	...	150–152	9.6	177
Tb(dpm)$_3$py	White	57.93	58.23	7.93	8.19	1.78	1.84	135–137	9.7	
Tb(dpm)$_3$dipy	White	59.71	59.81	7.58	7.61	3.24	3.27	195	9.7	
Tb(dpm)$_3$phen	Greenish white	60.80	61.27	7.37	7.56	3.15	3.22	241–242	9.7	
Dy(dpm)$_3$	White	55.65	55.96	8.07	8.40	...	...	182–183	10.3	173
Dy(dpm)$_3$py	White	57.67	57.95	7.77	8.10	1.77	1.98	135–137	10.7	
Dy(dpm)$_3$dipy	White	59.47	58.76	7.54	7.65	3.22	3.19	193	10.2	
Dy(dpm)$_3$phen	White	60.56	60.18	7.34	7.52	3.14	3.18	250	10.0	
Ho(dpm)$_3$	Yellowish white	55.46	55.67	8.04	8.25	...	...	178–180	10.0, 10.0	208
Ho(dpm)$_3$py	White	57.49	57.46	7.87	8.08	1.76	1.79	134–135	10.3	208
Ho(dpm)$_3$dipy	Light yellow	59.30	60.01	7.52	7.81	3.22	3.20	188–190	10.5	208
Ho(dpm)$_3$phen	Light yellow	60.39	61.07	7.32	7.58	3.13	3.13	246–248	10.3	208
Er(dpm)$_3$	Pink	55.28	54.89	8.01	8.20	...	...	179–180	9.3	187
Er(dpm)$_3$py	Pink	57.32	57.45	7.73	8.11	1.76	1.58	131–133	9.5	
Er(dpm)$_3$dipy	Pink	59.14	59.49	7.50	7.75	3.21	3.15	183	9.4	
Er(dpm)$_3$phen	Pink	60.24	60.79	7.30	7.53	3.12	2.97	254–256	9.5	
Tm(dpm)$_3$	White	55.15	55.30	7.99	8.24	...	...	170–173	7.2	152
Tm(dpm)$_3$py	White	57.21	57.27	7.83	8.00	1.76	1.65	134–136	...	
Tm(dpm)$_3$dipy	Light yellow	59.03	60.14	7.49	7.79	3.20	3.20	189–193		
Tm(dpm)$_3$phen	Light yellow	60.13	60.92	7.29	7.55	3.12	3.14	235–239	7.2	
Yb(dpm)$_3$	White	54.83	54.63	7.95	7.86	...	...	165–167	4.3, 4.3	173
Yb(dpm)$_3$py	White	56.91	56.85	7.79	7.97	1.75	1.62	130–132	4.5, 4.3	
Yb(dpm)$_3$dipy	White	58.75	58.69	7.45	7.69	3.19	3.22	167–168	4.3	
Yb(dpm)$_3$phen	White	59.85	60.63	7.26	7.62	3.10	3.11	...	4.3	
Lu(dpm)$_3$	White	54.69	54.35	7.93	8.00	...	...	173–174	Diamag	
Lu(dpm)$_3$py	White	56.78	55.54	7.77	7.74	1.74	1.62	125–127	Diamag	

[a] Dta and tga results generally support the melting point data and the former results may be obtained from the authors by those interested in the details. [b] Where there are two values listed, the first is the value obtained by the nmr technique and the second is the value obtained by the Gouy technique. Where there is only one value, the nmr technique was employed.

(dpm)$_3$dipy (M = same first 11 metals, but not Lu), M(dpm)$_3$phen (M = same first 11 metals, but not Lu), and Ce(dpm)$_4$. Elsewhere,[7] we shall deal with all of the various nmr studies involving these compounds and in particular their potential as proton shift reagents for various compounds. In this paper we describe the preparation and characterization of the lanthanide chelates and report the results of the nmr study of their magnetic moments and Weiss constants and of a low-temperature (77°K) study of their optical spectra.

Experimental Section

A. Preparation of Compounds. 1. The Tris(dipivaloylmethanato)metal(III) Compounds.—All 12 compounds (Pr–Lu, except Pm) were prepared by the method of Eisentraut and Sievers[8] and Berg and Acosta[9] with the difference that the compounds were purified by recrystallization three times from *n*-hexane rather than by sublimation. Results of elemental analyses are given in Table I along with other characterizing information. With cerium, the only product isolated had a 4:1 ligand-to-metal ratio and further experiments (*vide infra*) indicated that the product contains Ce(IV), leading to the simple formulation Ce(dpm)$_4$.

2. Pyridine Adducts of the Foregoing Compounds.—The 12 compounds (Pr–Lu, except Pm) were prepared by dissolving the tris(dipivaloylmethanate) in absolutely dry pyridine inside a drybox. The solution was left overnight in a tightly stoppered flask in the box. Then the excess pyridine was evaporated by evacuation in a vacuum desiccator. The dried product was dissolved in absolutely dry benzene and filtered, and the filtrate was evaporated to dryness in a vacuum desiccator. All operations were carried out in a dry, inert-atmosphere box. The compounds were stored in a desiccator over NaOH. Elemental analyses and other characterizing information are collected in Table I. The cerium compound, Ce(dpm)$_4$, did not yield a pyridine adduct.

3. 2,2′-Dipyridyl Adducts of the Tris(dipivaloylmethanates).—The 11 compounds (Pr–Yb, except Pm) were prepared by mixing in a 1:1 mole ratio the tris(dipivaloylmethanate) and the 2,2′-dipyridyl in the solvent carbon tetrachloride. Evaporation of the solvent yielded the desired 1:1 adduct, which was recrystallized three times from *n*-hexane. The cerium compound, as ex-

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pected, did not yield an adduct compound. Elemental analyses and other characterizing data are collected in Table I.

4. 1,10-Phenanthroline Adducts of the Tris(dipivaloylmethanates).—These 11 compounds (Pr–Yb, except Pm) were prepared by exactly the same procedure used for the 2,2′-dipyridyl adducts, and again the cerium compound did not yield an adduct compound. Elemental analyses and other characterizing data are collected in Table I.

B. Physical Chemical Methods. 1. Thermal Properties.—Melting points were determined with a Thomas-Hoover Capillary Unimelt melting point apparatus. Differential thermal analysis (dta) curves were obtained with a Du Pont 900 instrument, using a heating rate of 20°/min in a nitrogen atmosphere. Thermogravimetric analysis (tga) was performed with a Du Pont 950 instrument, with the sample heated at the rate of 10°/min in a nitrogen atmosphere.

2. Spectral Properties.—A Cary 14 spectrophotometer was used for obtaining low-temperature optical spectra. Samples mulled in Nujol were smeared on filter paper which was then mounted on a brass plate which dipped inside an optical dewar flask containing liquid nitrogen.

3. Magnetic Properties.—Magnetic susceptibilities were measured using a Gouy balance in the case of compounds which had been prepared in sufficient quantity to permit these measurements. However, magnetic susceptibility was measured for all of the compounds at ambient temperature using Evans' nuclear magnetic resonance method.[10] The solvent used to prepare the standard solutions was a 1:1 mixture of CCl_4 and $CHCl_3$. The data were corrected for the diamagnetism of the ligands. Weiss constants, Δ, were determined for ten of the compounds in 1:1 CCl_4 and CH_2Cl_2 by measuring the magnetic susceptibilities by the nmr technique at several (usually six) temperatures between −90 and +38°. Employing the equation $\chi = C/(T + \Delta)$, the Δ values were taken from graphical plots of $1/\chi$ *vs.* T.

Results and Discussion

The compounds which were prepared for this study are listed in Table I, along with certain characterizing information. All of the "adduct" or mixed-ligand compounds, *i.e.*, those with pyridine, 2,2′-dipyridyl, or 1,10-phenanthroline, are new. However, it should be pointed out that several analogous mixed-ligand complexes have previously been reported, for example, 1:1 or 1:2 adducts of $Eu(dbm)_3$ (dbm = dibenzoylmethanide ion) with a number of oxygen- and nitrogen-containing Lewis bases,[11] $Ln(dpm)_3 \cdot DMF$ complexes,[12] and a few adduct products which contain one molecule of either dipy or phen attached to tris(β-keto enolate)-lanthanide ions.[13–15]

Our compounds, however, are the first to contain these latter bidentate nitrogen donors complexed to tris(dipivaloylmethanates). In view of the rather bulky nature of the β-keto enolate ligands, it is somewhat surprising to find that an additional bidentate ligand can still attach to the tris(dipivaloylmethanate) lanthanide ion, raising its coordination number to 8. Nevertheless, not only does the addition occur, but the thermal data (melting points, differential thermal analyses curves, and thermogravmetric curves) show that these compounds are roughly as stable as analogous adduct complexes[11] with less bulky β-keto enolates.

It is interesting to note that the procedure used to obtain $M(dpm)_3$ complexes for all other lanthanides yields a Ce(IV) compound, $Ce(dpm)_4$, with this element. Perhaps this result is due to a combination of factors which include (a) the greater ease of oxidation [Ce(III) → Ce(IV)] in the case of cerium and (b) the more favorable total bond energy associated with the utilization of four rather than three bidentate ligands.

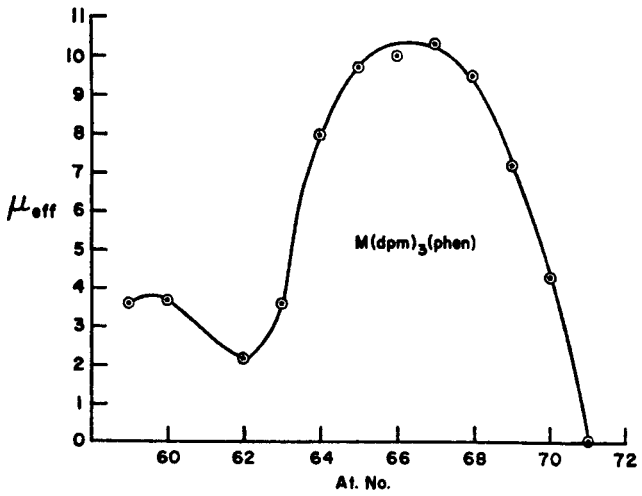

Figure 1.—Effective magnetic moments of the $M(dpm)_3$-phen complexes plotted *vs.* the atomic numbers of the metals, M.

TABLE II

OPTICAL SPECTRAL BANDS (CM^{-1}) OF PRASEODYMIUM COMPLEXES (GROUND STATE $^3H_4$)

$Pr(dpm)_3$	$Pr(dpm)_3dipy$	$Pr(dpm)_3phen$	$Pr(dpm)_3$ vapor[a]	Assignment[b]
		4,107 vw		
4,348 vvs		4,175 vvw		$^3H_6$
4,400 vs		4,405 m		
5,175 vvs		5,155 vw		
5,277 w		5,249 s	5,235	[$^3F_2$]
5,348 w		5,347 m		
5,806 s				
5,882 s				
5,917 s		5,952 vw		$^3F_3$
6,472 s				
6,579 s		6,579 s	6,578	
6,689 s		6,623 s		
6,969 s		6,981 m		
7,067 w		7,067 w		$^3F_4$
7,299 s		7,246 w		
8,403 m				$^1G_4$?
16,474 m	16,447 w	16,447 vw		
16,502 m				
16,543 m				
16,781 m	16,779 w	16,779 vw	16,835	
17,036 vvw				$^1D_2$
17,065 w	17,094 w	17,079 vw		
17,241 w		17,182 vw		
17,286 vw				
17,316 w			17,361	
			19,230 sh	
20,492 s		20,534 s	20,491 sh	$^3P_0$
20,534 s	20,555 s	20,619 vw		
20,929 m			20,920	
20,964 s				
21,110 m	21,075 m	21,097 s		$^3P_1$
21,142 w	21,119 vs			
21,231 w	21,322 m	21,322 s		
22,075 vs	22,272 m			
22,173 vm			22,123	$^3P_2$
22,421 w	22,523 s	22,523 m		

[a] Reference 13. [b] Assigned using collected data and assignments from G. H. Dieke, "Spectra and Energy Levels of Rare Earth Ions in Crystals," H. M. Crosswhite and H Crosswhite, Ed., Wiley, New York, N. Y., 1968. The brackets enclose the excited state of the "hypersensitive" transitions.

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TABLE III
OPTICAL SPECTRAL DATA FOR NEODYMIUM COMPLEXES (GROUND STATE $^4I_{9/2}$)

Nd(dpm)$_3$	Nd(dpm)$_3$ vapor[a]	Nd(dpm)$_3$dipy	Assignment[b]
	11,111		
11,494 vw	11,337	11,371 s	$^4H_{3/2}$
11,587 vw		11,501 m	
12,384 m	12,345	12,407 s	$^4F_{5/2}$
12,484 m	12,500	12,484 s	$^2H_{9/2}$
13,254 m			
13,319 m	13,297	13,351 m	$^4F_{7/2}$
13,432 m		13,441 m	
13,554 m	13,513	13,532 s	$^2S_{3/2}$
		15,873 vvw	$^2H_{11/2}$
	16,556 sh	16,708 m	
16,955 vs	16,883 sh	16,835 s	
17,050 vs	17,050	17,030 s	$^4G_{5/2}$, $^2G_{7/2}$
17,079 vs		17,138 vvs	
17,153 w		17,206 vs	
17,212 w		17,247 m	
17,247 s			
17,301 s		17,307 vs	
17,331 vs	17,346		
17,452 vvs		17,422 vvs	
18,832 s	18,779		
18,875 m	18,867	18,939 s	
18,957 w		18,975 vs	$^4G_{7/2}$
19,011 m		19,011 vs	
19,238 w		19,158 m	
19,417 vw		19,399 s	
19,531 w		19,493 s	$^2G_{9/2}$
		19,743 vw	
19,960 vw		19,861 vw	
20,812 vw		20,756 vw	
		20,877 w	$^4G_{9/2}$
		21,075 w	
		21,420 vw	
		21,786 w	
23,202 vw	23,148	23,148 m	$^2P_{1/2}$
27,739 vw			$^4D_{3/2}$
27,972 vw			
28,129 vw			$^4D_{5/2}$
28,288 vw			$2I_{11/2}$
28,506 vw			$^4D_{1/2}$

[a] Reference 13. [b] See footnote *b* of Table II.

TABLE IV
OPTICAL SPECTRAL BANDS (CM^{-1}) OF SAMARIUM (GROUND STATE $^6H_{5/2}$) AND ERBIUM (GROUND STATE $^4I_{15/2}$) COMPLEXES

Sm(dpm)$_3$	Sm(dpm)$_3$ vapor[a]	Assignment[b]	Er(dpm)$_3$	Er(dpm)$_3$ vapor[a]	Assignment[b]
	6,289	[?][c]		6,578	$^4I_{13/2}$
	6,578		6,756 vw	6,756	
	6,993				
	7,462 sh			9,900	
				10,152	$^4I_{11/2}$
8,104	8,064			10,257	
8,183		$^6F_{7/2}$			
8,222 m				12,658	$^4I_{9/2}$
9,268 w	9,174		15,186 w		
9,330 w	9,293	$^6F_{9/2}$	15,244 vw	15,384	$^4F_{9/2}$
9,379 w	9,469		15,279 w	15,527	
17,737 vw		$^6G_{5/2}$	18,657 vw	18,518 sh	
			18,692 vw		$^4S_{3/2}$
18,939 w			18,727 vw	18,726	
18,961 w		$^6F_{3/2}$			
			18,957 s		
19,900 w			18,993 *vvs*		
20,052 w		$^6G_{7/2}$	19,048 s		[$^2H_{11/2}$]
			19,128 vs		
20,358 w			19,157 vs	19,157	
20,408 w	20,408	$^4I_{9/2}$			
			20,367 w		
20,929 vw		$^6M_{15/2}$, $^4I_{11/2}$	20,429 vw		
20,986 vw			20,492 vw	20,491	$^4F_{7/2}$
			20,525 vw		
21,400 vw	21,367 sh		20,576 vw		
21,645 vw		$^4I_{13/2}$			
			22,099 vw		
22,198 vw		$^6F_{5/2}$, $^6G_{9/2}$	22,124 vw		$^4F_{3/2}$, $^4F_{5/2}$
22,272 vw					
			24,510 vw		
23,742 vvs	22,935		24,570 vw		
23,895 m	23,809	$^6P_{5/2}$	24,600 vw	24,630	$^2H_{9/2}$
24,085 m				25,316 sh	
				25,773	
24,540 m					
24,649 vs		$^6P_{3/2}$, $^4I_{15/2}$	26,178 vvs	26,178	
24,759 vs			26,281 vs		$^4G_{11/2}$
			26,385 vs	26,385	
24,863 w					
24,900 w		$^6F_{9/2}$	27,285 m	26,809 sh	$^2G_{9/2}$
25,013 w				27,100 sh	
26,137 w			27,510 w	27,397 sh	$^2K_{15/2}$
26,385 w					
26,490 m			27,663 w		$^2G_{7/2}$
26,560 m		$^6K_{11/2}$			
26,666 m					
27,360 s					

[a] Reference 13. [b] See footnote *b* of Table II. [c] These bands fit no previous assignments.

We have much evidence that we are indeed dealing with Ce(IV) and not Ce(III), as *might* have formed if one of the four β-diketone molecules were still retaining its acidic proton. This evidence includes its diagmagnetism, its nmr spectrum which fails to show any unique acidic proton and which shows all β-keto enolate ligands to be equivalent, the failure of the compound to yield any adducts with py, dipy, or phen, the intense color and particular optical spectrum of the compound (no sharp bands, but rising absorption in the visible toward a charge-transfer peak in the ultraviolet), and its similarity in both color and melting point to the product reported earlier[6] and also formulated as Ce(dpm)$_4$. The melting points for the M(dpm)$_3$ compounds range from a high of 222° (for M = Pr) to a low of 165° (for M = Yb), whereas the Ce(dpm)$_4$ compound melts at 276°.

The new monopyridine compounds all melt at 134 ± 4°, except for the lutetium compound which melts at 125°. The new dipyridyl compounds melt at 189 ± 6°, except for the ytterbium compound which melts at 167°. The new 1,10-phenanthroline compounds from Pr to Gd melt at 221 ± 4° and from Tb to Yb melt higher at 245 ± 10°.

Although it is always risky speculating on the significance of melting points, it does appear clear that in the four series of complexes (plus Ce(dpm)$_4$) the melting points increase in the order M(dpm)$_3$py < M(dpm)$_3$dipy < M(dpm)$_3$phen < Ce(dpm)$_4$. This order suggests that the seven-coordination species forms the least thermally stable lattice followed by the six-coordination species, which is less stable than the eight-coordination species. It is not clear to us, however, why the 1,10-phenanthroline compounds melt higher than the dipyridyl ones. Perhaps the rigidly planar phen ligand, which in its planarity is like the skeletal β-keto enolate anion, permits a more stable crystal packing. This suggestion is supported by the fact that the Ce(dpm)$_4$ compound has the highest melting point of all.

The magnetic moments, corrected for the diamagnetism of the ligands, are also listed in Table I. Most of the values are from nmr measurements and these compare well with the Gouy-determined values where the amount of sample permitted the latter determination to be made. If the values are plotted *vs.* increasing atomic number, the characteristic unequal double-humped curve (Figure 1) is obtained. The nmr technique for obtaining magnetic moments[10] thus has prov-

TABLE V

OPTICAL SPECTRAL BANDS (cm^{-1}) OF HOLMIUM (GROUND STATE $^5I_8$), DYSPROSIUM (GROUND STATE $^6H_{15/2}$), GADOLINIUM (GROUND STATE $^8S_{7/2}$), AND TERBIUM (GROUND STATE $^7F_6$) COMPLEXES

Ho(dpm)$_3$	Ho(dpm)$_3$ vapor	Assignment[b]	Dy(dpm)$_3$	Dy(dpm)$_3$ vapor[a]	Assignment[b]
15,420 m	15,537			7,836	[$^6F_{11/2}$]
15,468 m					
15,564 m		$^5F_5$		7,936 sh	?
15,625 m					
15,686 m				9,090	$^6H_{7/2}$, $^6F_{9/2}$
	17,497				
18,446 vw	18,181 sh	$^5S_2$		10,695	$^6H_{5/2}$ or $^6F_{7/2}$
18,553 s	18,518			11,111	$^6F_{7/2}$
18,584 s		$^5F_4$			
18,612 s				12,345	$^6F_{5/2}$
18,681 s					
				17,605	?
20,437 vw					
20,488 m			21,017 vw		
20,542 m	20,512	$^5F_3$	21,030 vw		$^4F_{9/2}$
20,653 w			21,313 vw		
20,674 m			21,468 vw		
20,747 w					
			21,949 m		
20,942 vw			22,036 m	22,026	
21,151 w		$^5F_2$	22,065 m		
			22,134 m		$^4I_{15/2}$
21,186 w			22,198 m		
21,345 m			22,336 vw		
21,390 w			22,386 vw		
21,436 vw					
21,552 m		$^5K_8$	23,392 vw		$^4G_{11/2}$
21,575 vw			23,474 vw		$^4G_{11/2}$
21,687 m	21,645				
21,805 w			24,802 vw		
21,858 w			24,925 vw		
			25,013 vw		
21,915 s	21,905 sh		25,100 vw		
21,954 w			25,176 vw		
21,973 s	21,978 sh				
21,997 s			25,465 w		
22,085 s		[$^5G_6$]	25,562 m		
22,139 s			25,674 m		
22,193 vs					
22,267 s			25,940 vs		
22,316 vvs	22,321				
23,474 w			17,265 m		$^5D_0$
23,657 w	23,584 sh				
23,725 vw			18,779 m	18,656	
23,753 w	23,752	$^5G_5$	18,847 vw		$^5D_1$
23,866 m			18,986 vw		
23,895 m			19,029 vw		
23,952 m					
24,038 w			21,450 m		
			21,501 vs	21,482	[$^5D_2$]
25,820 vw	25,706		21,529 vs	21,598	
25,853 vw		$^5G_4$			
25,887 m			Gd(dpm)$_3$		Assignment
26,130 s	26,178	$^8K_7$	31,847 w		$^6P_{7/2}$
27,532 w			36,364 m		$^6I_{9/2}$, $^6I_{17/2}$
27,412 w					
27,472 s			37,106 m		$^6I_{15/2}$ $^6I_{13/2}$
27,594 w		$^3H_6$, $^3G_5$			
27,693 s			40,816 m		$^6D_{9/2}$
27,755 s					
			Tb(dpm)$_3$		Assignment
			28,653 m		$^5D_2$, $^5G_4$, $^5L_6$
			31,008		

[a] Reference 13 [b] See footnote *b* of Table II

en quite satisfactory with lanthanide complexes and so we extended its use to the evaluation of Weiss constants by carrying out the measurements for at least six temperatures between −90 and +38° for each of ten compounds To our knowledge this is the first time such use has been made of the nmr technique The compounds studied this way and their Weiss constants are listed in Table I It was our intention to try to find some relationship between the magnetic properties of these complexes and their abilities as proton nmr (pseudocontact) shift reagents This will be explored elsewhere[7] in the discussion of the nmr shift studies

The 77°K optical spectral data for M(dpm)$_3$ (M = Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm), Pr(dpm)$_3$-(*o*-phen), Pr(dpm)$_3$phen, and Nd(dpm)$_3$dipy are collected in Tables II–V. Included are the data obtained by Gruen, DeKock, and McBeth[16] on eight of the M-(dpm)$_3$ compounds in the vapor phase Assignments are made of most of the bands to transitions from the indicated ground level to the appropriate indicated SLJ level The so-called "hypersensitive" transitions, *i.e*, those whose intensities (in eight of the rare earths) are particularly and strongly dependent upon media, are bracketed in Tables II–V Further interpretation of the optical spectral data is not warranted at this time, but a future paper will deal with the emission spectra of several of the complexes reported here

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Nuclear Magnetic Resonance Spectra of Tris[2,2,6,6-tetramethyl-3,5-heptanedionato] Complexes of the Lanthanides. Temperature Dependence of Shift Reagents

Sir:

Study of the tris[2,2,6,6-tetramethyl-3,5-heptanedionato] (tris(dpm)) chelates of the rare earth elements by nmr has been biased heavily toward the tris(dpm) derivative of europium,[1,2] which has enjoyed spectacular success as a deshielding shift reagent; the analogous derivative of praeseodymium, capable of displacing the signals of a sample to higher field with only a slight increase of line width, has also been studied,[3,4] and recent comparative studies have shown that the former complex displays superior magnetic[5] and solubility[6] properties. As tris(dpm) derivatives have been prepared[7] from the entire rare earth group (except cerium and promethium), we undertook to measure the nmr parameters of *tert*-butyl protons of these chelates, both alone and in the presence of potential ligands. Cyclohexanone or 1-hexanol as ligand produced approximately equal changes in chemical shift of the *tert*-butyl resonances of any given complex, although the magnitude and direction of such changes varied broadly from one central atom to the next (Table I). Table II details the concomitant alterations produced in the 100-MHz nmr spectrum of cyclohexanone. The direction of displacement is also a function of the central atom, and the magnitude of this effect, which varies from slight (Sm) to enormous (Dy, Ho), is nearly linear with the proportion[1,4,6] of complex present; the extent of broadening of signals is essentially a function only of the central atom. Direct measurements of relaxation times of the complexes are in progress. (Also under current investigation are the dipyridyl and 1,10-phenanthroline 1:1 adducts of the tris(dpm) compounds of the entire rare earth series for the purpose of relaxation studies.)

In general, the solubility of all 12 compounds in carbon tetrachloride is modest at best, and, as noted for the Eu analog, enhanced somewhat by the presence of a coordinating substrate; Ho and, to a lesser extent, Dy are slight exceptions in being rather less insoluble. Solutions of complexes in the present study were prepared by dissolving 15 ± 3 mg of the appropriate solid in 0.3 ml of warmed carbon tetrachloride that had been stored for at least 1 week over NaOH pellets.

It was found that the use of untreated CCl_4 as a solvent for such studies promoted decomposition of at least several of the complexes; the *tert*-butyl resonances of solutions of $Pr(dpm)_3$, $Nd(dpm)_3$, and $Sm(dpm)_3$ in untreated carbon tetrachloride were shown to diminish upon standing and/or dilution, with concurrent appearance of a second signal. During investigation of this phenomenon, it was further noted that these signals displayed substantial shifts of field

Table I. Chemical Shifts and Line Widths (at Half-Height) of the *tert*-Butyl Proton Signals of $M(dpm)_3$ in CCl_4, in the Presence of Oxygen-Containing Species

	Ligand					
	None		Cyclohexanone		1-Hexanol	
M	Ppm[a]	Width[b]	Ppm[a]	Width[b]	Ppm[a]	Width[b]
Pr	0 6	40	2 8	2		
Nd	0 8	16	2 1	10		
Sm	1 08	7	1 2	6		
Eu	0 48	10	−0 5	5	−0 6	20
Gd	0 9	1500	1 8	800		
Tb	17 4	250	16 0	170	17 7	60
Dy	17 7	180	21 9	130	20 3	120
Ho	5 3	180	7 3	180	8 8	180
Er	−3 6	250	−6 2	70	−5 5	45
Tm	12 8	400	15 2	240	17 9	170
Yb	−0 3	60	−1 9	20		
Lu	1.14					

[a] Downfield from TMS. [b] In hertz, approximately

Table II. Chemical Shifts and Line Widths (at Half-Height) of Signals of the α-, β-, and γ-Methylene Protons of Cyclohexanone (0.1 *M*) in a Saturated Solution[a] of $M(dpm)_3$ in CCl_4

	α		β		γ	
M	δ[b]	Width[c]	δ[b]	Width[c]	δ[b]	Width[c]
Pr	−8 8	(>20)[d]	−2 8	(~20)[d]	−2 0	(~20)[e]
Nd	−3 1	(>20)[e]	−0 4	(>20)	−0 1	(>20)
Sm[g]	~1 1	(>20)[e]	~1 1	(>20)	~1 1	(>20)
Eu	5 4	(~15)[d]	3 8	(~15)[d]	3 5	(~15)[e]
Gd[f]						
Tb	−23 8	(75)	−12 4	(32)	−9 2	(24)
Dy	−51 6	(85)	−21 2	(25)	−16 2	(21)
Ho	−49 0	(92)	−21 6	(29)	−16 4	(22)
Er	28 0	(61)	13 0	(>20)	10 5	(>20)
Tm[h]	−42 2	(90)	−17 3	(38)	−13 1	(34)
Yb	14 6	(23)	7 4	(>20)	6 1	(>20)
None	2 45(	~15)[d]		~2 00	1 70	

[a] Except Ho, which is much more soluble, $[M(dpm)_3]$ is slightly less than 0.1 *M*. [b] In parts per million. [c] In hertz [d] Sufficiently resolved to permit identification of multiplicity [e] Evidence of fine structure, but not resolved enough for identification [f] Not observed; overlap possible as *tert*-butyl resonance is very broad [g] These values were determined by adding cyclohexanone and observing emergence of resonances from beneath the *tert*-butyl signal [h] These values are reversed in sign from analogous data reported by Hart, *et al.*,[3] for $Tm(ClO_4)_3[OP(NMe_2)_3]_4$ in acetonitrile, but similar reversals have been produced (E R Birnbaum and T Moeller, *J Amer. Chem Soc.*, **91**, 7274 (1969)) by altering ligands in Pr and Nd complexes.

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(7) J Selbin, N Ahmad, and N. S. Bhacca, *Inorg Chem*, in press

position (on the order of several parts per million, reversible on cooling) as the probe temperature was increased gradually to about 75°. We prepared a sample of 2-heptanone (~0.1 *M*) in carbon tetrachloride, added the maximum amount of $Eu(dpm)_3$, and recorded the nmr spectrum of the sample at temperatures throughout the liquid range of CCl_4. Proportional enhancement of all signals in the substrate is observed (Table III) as the sample temperature is lowered,

Table III. Temperature-Dependent Chemical Shifts[a] of Protons of 2-Heptanone in CCl_4 Containing $Eu(dpm)_3$

T, °C	C-7	C-6	C-5	C-4	C-1	C-3
−30[b]	1 06	1 48	2 12	2 93	3 71	3 99
−12	1 04	1 44	2 04	2 81	3 52	3 82
0	1 02	1 38	1 93	2 55	3 25	3 55
35	1 01	1 37	1 91	2 49	3 18	3 48
66	0 99	1 32	1 75	2 28	2 93	3 23
Ref[c]	0 90	1 19	~1 39	~1 55	2 01	2 31

[a] Parts per million [b] Freezing occurs after a few minutes [c] 2-Heptanone in CCl_4

and suggests possible utility of reduced temperature determinations in cases where the limited solubility of the lanthanide complex is inadequate, or of variable temperature studies in lieu of measurements at a number of different relative concentrations.

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Naseer Ahmad, N. S. Bhacca,* J. Selbin, J. D. Wander
Coates Chemical Laboratory, Louisiana State University
Baton Rouge, Louisiana 70803
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Transition-metal Complexes Containing Phosphorus Ligands. Part VII.[1] New and Improved Syntheses of Some Triphenylphosphine Complexes of Rhodium, Iridium, Ruthenium, and Osmium

By N. Ahmad, S. D. Robinson,* and M. F. Uttley, Department of Chemistry, King's College, Strand, London WC2R 2LS

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Transition-metal Complexes Containing Phosphorus Ligands. Part VII.[1] New and Improved Syntheses of Some Triphenylphosphine Complexes of Rhodium, Iridium, Ruthenium, and Osmium

By N. Ahmad, S. D. Robinson,* and M. F. Uttley, Department of Chemistry, King's College, Strand, London WC2R 2LS

Previously reported, convenient, single-stage syntheses for important hydride, carbonyl, and nitrosyl containing triphenylphosphine complexes of the platinum group metals have been further improved by use of ethanolic potassium hydroxide or triethylamine in place of sodium borohydride as basic reducing agent. The technique has also been extended to include convenient new syntheses for the ruthenium and osmium triphenylphosphine derivatives. *cis*-$RuCl_2(CO)_2(PPh_3)_2$, $OsHCl(CO)(PPh_3)_3$, $OsH_2(CO)(PPh_3)_3$, and $OsH_2(CO)_2(PPh_3)_2$. The stereochemistry of these last-named complexes is discussed. Attempts to extend this mode of synthesis to include derivatives of other triarylphosphines are described. New complexes synthesised include $Rh(NO)L_2$[L = P(*p*-$C_6H_4Cl)_3$ and P(*p*-$C_6H_4Me)_3$] and $Ru(CO)_3L_2$ [L = P(*p*-$C_6H_4Me)_3$ and P(*p*-$C_6H_4OMe)_3$]

In a previous publication [2] we described a technique for the convenient, single-stage synthesis of numerous triphenylphosphine derivatives of the platinum metals containing carbonyl, nitrosyl, or hydride ligands. We now report improvements and extensions to these syntheses; in particular we describe alternative, more convenient and efficient reagents capable of replacing sodium borohydride in these reactions. The efficiency of a series of base–alcohol reducing systems involving sodium carbonate, sodium formate, triethylamine and potassium hydroxide was examined. Potassium hydroxide–alcohol was found to be a particularly effective reducing system and its use permitted extension of our general technique to include simple, convenient syntheses of several important osmium carbonyl hydride derivatives, previously accessible only by much more tedious routes. We also sought extension of the syntheses to include preparation of platinum group metal complexes containing other triarylphosphine ligands. Only a small proportion of the large number of syntheses attempted using these latter phosphines gave the desired products in satisfactory yield and purity. The remaining syntheses were unsatisfactory for a variety of reasons including poor yields, irreproducibility, and formation of impure or mixed products. No single reason can be cited for these failures; however, solubility differences, arising from changes in the triarylphosphine employed, are expected to influence the course of these solubility-controlled reactions and are therefore probably a major contributory factor.

Synthesis.—The literature relating to previous syntheses of *cis*-$RuCl_2(CO)_2(PPh_3)_2$, $OsHCl(CO)(PPh_3)_3$, $OsH_2(CO)(PPh_3)_3$, and $OsH_2(CO)_2(PPh_3)_2$ is summarised below; similarly surveys for other complexes mentioned in this work were provided in our earlier paper [2] on synthesis technique and are, therefore, not repeated here.

The *cis*-isomer of $RuCl_2(CO)_2(PPh_3)_2$ synthesised in this work has previously been prepared by reaction of various ruthenium carbonyl halide species including $[RuCl_2(CO)_2]_n$,[3] $[RuCl_4(CO)_2]^{2-}$,[4] and $RuCl_2(CO)_3$(tetrahydrofuran) [5] with triphenylphosphine. The same complex has also been obtained by carbonylation of $RuCl_2(PPh_3)_4$.[6] Several other *cis*- and *trans*-isomers have also

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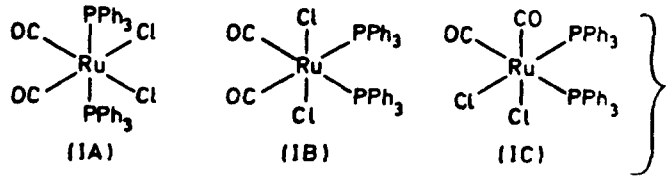
been reported. The new single-step synthesis, which involves formation of $Ru(CO)_3(PPh_3)_2$ and subsequent reaction *in situ* with carbon tetrachloride, affords the required complex in high yield and purity. The osmium triphenylphosphine derivatives discussed in this paper have all been characterised previously. $OsHCl(CO)(PPh_3)_3$ was first prepared by Vaska [7,8] and was subsequently correctly formulated as a carbonyl hydride derivative of osmium(II).[9,10] Synthesis was first achieved by prolonged reaction of ammonium chloro-osmate(IV) and triphenylphosphine in a high-boiling alcoholic solvent, and this technique is in current use.[11] The carbonyl dihydride, $OsH_2(CO)(PPh_3)_3$, has previously been obtained by a two-step process involving treatment of the hydridochloride, $OsHCl(CO)(PPh_3)_3$, with alcoholic base.[12] The dicarbonyldihydride, $OsH_2(CO)_2(PPh_3)_2$, has previously been prepared [13] by reacting preformed $OsH_2(CO)_4$ with triphenylphosphine in refluxing tetrahydrofuran for 12 hours; it has also been obtained [13] in 50% yield by high-pressure hydrogenation of $Os(CO)_3(PPh_3)_2$. The new syntheses described below offer a substantial improvement in speed and efficiency over those currently available. In each case solutions of sodium chloro-osmate, formaldehyde, and, if required, potassium hydroxide are added to a vigorously stirred, boiling solution of triphenylphosphine in 2-methoxyethanol. The syntheses of $OsH_2(CO)(PPh_3)_3$ and $OsH_2(CO)_2(PPh_3)_2$ are performed under very similar conditions; use of a large excess of triphenylphosphine suppresses carbonylation and affords the former, while the latter is prepared in the presence of excess of aqueous formaldehyde and a deficiency of phosphine. The synthesis of $Ru(NO)_2(PPh_3)_2$ by the single-step technique affords the best results when triethylamine rather than potassium hydroxide is used in place of sodium borohydride. Many of the other syntheses described in this paper will also proceed, though usually somewhat less efficiently, when potassium hydroxide is replaced by sodium carbonate, sodium formate, or triethylamine. The apparatus and general technique employed in these syntheses are essentially identical with those described in our previous publication.[8] Minor modifications leading to improved yield or purity for certain products are given in the Experimental section. Once again we stress the importance of achieving and maintaining homogeneous reaction conditions wherever possible by efficient stirring and rapid, successive addition of reagents.

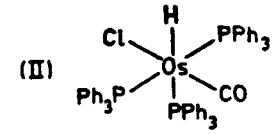
Structural features.—Evidence concerning structure and stereochemistry of the ruthenium derivatives, *cis*-$RuCl_2(CO)_2(PPh_3)_2$, and the osmium derivatives $OsHCl(CO)(PPh_3)_3$, $OsH_2(CO)(PPh_3)_3$, and $OsH_2(CO)_2(PPh_3)_2$ is discussed below; similar discussion relating to other complexes mentioned in this work was given in our previous paper [8] and is, therefore, not repeated here.

The ruthenium dicarbonyl complex, $RuCl_2(CO)_2(PPh_3)_2$ may exist in five stereoisomeric forms; three of these (IA)—(IC) possess a pair of *cis*-carbonyl ligands. The isomer prepared in our synthesis [ν(CO) 2065(s) 1998(s) cm^{-1}] has previously been assigned structures (IA),[6] and (IB),[8] on the basis of circumstantial evidence

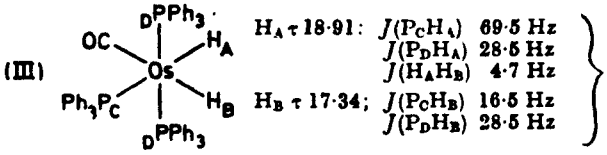


derived from dipole moment and proton n.m.r. data. However a more recent paper [14] assigns stereochemistry (IA) to a new *cis*-dicarbonyl isomer, $RuCl_2(CO)_2(PPh_3)_2$ [ν(CO) 2043 and 1979 cm^{-1} (CH_2Cl_2)], and proposes stereochemistry (IB) or (IC) for the isomer identical with that prepared in the present study.

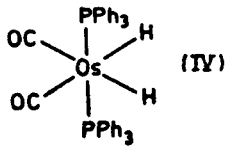
The high-field n.m.r. spectrum of the osmium complex, $OsHCl(CO)(PPh_3)_3$, recorded here for the first time, shows a doublet of triplets [$J(P_tH) = 87{\cdot}0$ Hz; $J(P_cH) = 24{\cdot}5$ Hz] centred at τ 16·27; this data confirms for $OsHCl(CO)(PPh_3)_3$ in solution, a structure (II) similar to that found [15] by *X*-ray crystallography for the related bromo-derivative in the solid state.



The high-field n.m.r. spectrum of $OsH_2(CO)(PPh_3)_3$ comprises two first-order patterns of 12 lines each and confirms the stereochemistry (III) previously suggested on



the basis of i.r. data alone.[12] The structure (IV) has previously been proposed for $OsH_2(CO)_2(PPh_3)_2$ on the



basis of high-field n.m.r. data [triplet τ 17·65, $J(PH) = 23$ Hz].[13] Our n.m.r. data for this complex [triplet τ

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17·08, J(PH) = 22·75 Hz] differ slightly from those previously recorded but confirm the stereochemistry suggested.

EXPERIMENTAL

Microanalyses were performed by Dr. Strauss at Oxford and Dr. Bernhardt at Mulheim, Germany. I.r. spectra were recorded as Nujol mulls on a Perkin-Elmer 457 grating spectrometer and calibrated using polystyrene film. N.m.r. spectra were recorded on a Varian HA 100 spectrometer. Melting points were all accompanied by a degree of decomposition and were measured in air (Kofler hot stage) and in a sealed capillary under nitrogen (Buchi melting point apparatus). Platinum metal salts were purchased from Johnson Matthey; hydrated ruthenium trichloride was used as purchased and may have contained appreciable amounts of ruthenium(IV) species. Other reagents and solvents were purchased from B.D.H. and used without further purification.

All reactions were performed under oxygen-free nitrogen.

Preparation of Complexes.—General observations. The success of the following preparations depends, in almost every instance, upon the maintenance of essentially homogeneous reaction conditions until precipitation of product occurs and reaction is complete. This requires the addition of the various reagent solutions *rapidly* and *successively* to the vigorously boiling reaction mixture, and failure to observe this precaution leads to precipitation of insoluble intermediates which may fail to react further, and thus contaminate the product. The reactions are conveniently performed in a 250 ml conical flask fitted with a condenser, a nitrogen inlet, and a port for introduction of reagent solutions. The reaction solutions are stirred magnetically. The products were frequently deposited in an analytically and spectroscopically pure state, and were merely washed; further purification was achieved where necessary by application of literature methods. The use of these reactions for large-scale syntheses has not been investigated; difficulties in achieving and maintaining homogeneous reaction conditions may be encountered when attempting to scale up the preparations.

Rhodium Complexes.—Hydridotetrakis(triphenylphosphine)rhodium. Solutions of hydrated rhodium trichloride (0·26 g, 1·0 mmol) in warm ethanol (20 ml) and potassium hydroxide (0·4 g) in warm ethanol (20 ml) were added in rapid succession to a vigorously stirred solution of triphenylphosphine (2·62 g, 10 mmol) in boiling ethanol (80 ml). The mixture was heated under reflux for 10 min, cooled to 30°, filtered, and the precipitate washed with ethanol, water, ethanol, and finally n-hexane; it was then dried *in vacuo* to give the required product as yellow microcrystals (0·88 g, 77%), m.p. 145—147° in air, 154—156° under nitrogen (Found: C, 74·7; H, 5·3; P, 10·5. Calc. for $C_{72}H_{61}P_4Rh$: C, 75·0; H, 5·35; P, 10·75%).

Hydridocarbonyltris(triphenylphosphine)rhodium. A solution of hydrated rhodium trichloride (0·26 g, 1·0 mmol) in ethanol (10 ml) was added to a vigorously stirred solution of triphenylphosphine (2·62 g, 10 mmol) in boiling ethanol (100 ml). After a delay of 15—20 s, aqueous formaldehyde (10 ml, 40% w/v soln.) and a solution of potassium hydroxide (0·8 g) in ethanol (20 ml) were added rapidly and successively to the vigorously stirred, boiling reaction mixture and the whole was heated under reflux for 10 min; it was then allowed to cool to 30°. The crystalline product was filtered off and washed with ethanol, water, ethanol, and finally n-hexane; it was then dried *in vacuo* to give yellow microcrystals (0·85 g, 94%), m.p. 120—122° in air, and 172—174° under nitrogen (Found: C, 72·1; H, 5·15; P, 9·85. Calc. for $C_{55}H_{46}OP_3Rh$: C, 71·9; H, 5·05; P, 10·1%).

Nitrosyltris(triphenylphosphine)rhodium. Solutions of hydrated rhodium trichloride (0·13 g, 0·5 mmol) in ethanol (10 ml) and *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide (0·2 g) in ethanol (50 ml) were added rapidly and successively to a vigorously stirred, boiling solution of triphenylphosphine (1·31 g, 5 mmol) in ethanol (40 ml). The mixture was boiled for a further 2 min, cooled to 30°, filtered, and the precipitate washed with ethanol, water, ethanol and finally n-hexane; it was then dried *in vacuo* to give the required product as red crystals (0·43 g, 95%), m.p. 160° in air, 205—206° under nitrogen (Found: C, 70·6; H, 4·7; P, 10·35; N, 1·5. Calc. for $C_{54}H_{45}NOP_3Rh$: C, 70·45; H, 4·75; P, 9·85; N, 1·4%.

Nitrosyltris(tri-p-tolylphosphine)rhodium. This complex was similarly prepared using tri-*p*-tolylphosphine; after evaporation of the reaction solution to small volume under nitrogen it deposited the compound as dark red microprisms (60%), ν(NO) 1602 cm^{-1}, m.p. 140—143° in air, 208—209° under nitrogen (Found: C, 72·1; H, 6·2; N, 1·55; P, 8·6. $C_{63}H_{63}NOP_3Rh$ requires C, 72·35; H, 6·05; N, 1·35; P, 8·9%).

Nitrosyltris(tri-p-chlorophenylphosphine)rhodium. This complex was similarly prepared using tri-*p*-chlorophenylphosphine; it was deposited from the reaction solution as red-brown *microcrystals* (80%) ν(NO) 1598 cm^{-1}, m.p. 100—106° in air (Found: C, 52·45; H, 3·15; N, 1·3;. $C_{54}H_{36}Cl_9NOP_3Ph$ requires C, 52·61; H, 2·95; N, 1·15%).

Iridium Complexes mer- *and* fac-*Trihydridotris(triphenylphosphine)iridium.*—Sodium hexachloroiridate (1·68 g, 3·0 mmol) was dissolved in ethanol (30 ml) with gentle warming; the solution was then filtered. The filtrate and a solution of sodium borohydride (0·6 g) in ethanol (60 ml) were added in rapid succession to a boiling solution of triphenylphosphine (6·3 g, 24 mmol) in ethanol (240 ml). *There was much frothing and evolution of hydrogen on addition of the sodium borohydride solution.* The mixture was heated under reflux for 15 min and then allowed to cool to 55°; it was immediately filtered. The filtrate was retained for subsequent isolation of the *fac*-isomer.

The precipitated, impure *mer*-isomer was washed with ethanol (55°), water, ethanol, and finally n-hexane and then dried *in vacuo*. Traces of *fac*-isomer were removed by boiling the complex in a small volume of ethanol and filtering the suspension at the boiling point. Microcrystals of pure *mer*-isomer were dried *in vacuo* (1·04 g, 36%), m.p. 192—193° in air 228—230° sealed under nitrogen (Found: C, 65·9; H, 5·1; P, 9·3. Calc. for $C_{54}H_{48}IrP_3$: C, 66·05; H, 4·95; P, 9·45%). *mer*-Trihydridotris(triphenylphosphine)-iridium may be further recrystallised from benzene–methanol when it forms a 1 : 1 benzene adduct (Found: C, 67·8; H, 5·15; P, 8·3. Calc. for $C_{60}H_{54}IrP_3$: C, 67·95; H, 5·15; P, 8·75%).

The filtrate retained from the synthesis of *mer*-$IrH_3(PPh_3)_3$ was concentrated under reduced pressure to obtain the *fac*-isomer. The crude material thus deposited was washed with ethanol, water, and ethanol then, repeatedly, with hot n-hexane; it was finally dried *in vacuo* to afford *fac*-$IrH_3(PPh_3)_3$, practically free from *mer*-isomer (yield 1·31 g, 45%). Recrystallisation from benzene–methanol

yielded pure *fac*-trihydridotris(triphenylphosphine)iridium as white microcrystals, m.p. 168—171° in air, 208—218° sealed under nitrogen (Found: C, 65·85; H, 4·9; P, 9·05. Calc. for $C_{54}H_{48}IrP_3$: C, 66·05; H, 4·95; P, 9·45%).

Hydridocarbonyltris(triphenylphosphine)iridium. Solutions of sodium hexachloroiridate (0·84 g, 1·5 mmol) in warm 2-methoxyethanol (30 ml), aqueous formaldehyde (15 ml, 40% w/v soln.), and potassium hydroxide (0·5 g) in 2-methoxyethanol (30 ml) were added in rapid succession to a vigorously stirred, boiling solution of triphenylphosphine (2·37 g, 9·0 mmol) in 2-methoxyethanol (90 ml). The solution was heated under reflux for 15 min, allowed to cool, and then diluted with methanol (20 ml). The crystalline product was filtered off, washed with ethanol, water, ethanol, and finally n-hexane; it was then dried *in vacuo* (1·35 g, 95%), m.p. 166—167° in air, 216—218° sealed under nitrogen (Found: C, 65·6; H, 4·75; P, 9·05. Calc. for $C_{55}H_{46}IrOP_3$: C, 65·53; H, 4·6; P, 9·2%).

*Hydridocarbonyltris(tri-*p*-tolylphosphine)iridium.* This complex was similarly prepared using tri-*p*-tolylphosphine and was induced to crystallise from the reaction solution by addition of a small volume of water. The precipitated product was washed with water followed by minimal volumes of ethanol and n-hexane; it was then dried *in vacuo* to give yellow microcrystals (50%); ν(IrH) 2060m and ν(CO) 1925vs cm^{-1}; m.p. 141—142° in air 162—163° under nitrogen (Found: C, 68·35; H, 5·9; P, 8·0. $C_{64}H_{64}IrOP_3$ requires C, 67·75; H, 5·7; P, 8·2%).

Ruthenium Complexes.—Dichlorodicarbonylbis(triphenylphosphine)ruthenium (*cis*-carbonyl ligands). To a boiling solution of triphenylphosphine (0·78 g, 3·0 mmol) in 2-methoxyethanol (20 ml) were added successively a solution of hydrated ruthenium trichloride (0·13 g, 0·5 mmol) in 2-methoxyethanol (10 ml), aqueous formaldehyde (5 ml, 40% w/v soln.), potassium hydroxide (0·2 g) in 2-methoxyethanol (10 ml) and, finally, neat carbon tetrachloride (5 ml). The mixture was heated under reflux for 30 min, cooled, and diluted with methanol (30 ml). The precipitated product was washed with ethanol, water, and ethanol, and then recrystallised from dichloromethane–methanol to give white crystals (0·255 g, 68%), m.p. 233—236° in air (Found: C, 60·65; H, 4·25; P, 8·2. Calc. for $C_{38}H_{30}Cl_2O_2P_2Ru$: C, 60·65; H, 4·0; P, 8·25%).

Dihydridocarbonyltris(triphenylphosphine)ruthenium. Method a. Solutions of hydrated ruthenium trichloride (0·13 g, 0·5 mmol) in ethanol (10 ml), aqueous formaldehyde (5 ml, 40% w/v soln.), and potassium hydroxide (0·2 g) in ethanol (10 ml) were added successively to a boiling solution of triphenylphosphine (0·78 g, 3 mmol) in ethanol (30 ml). The mixture was heated under reflux for 5 min, cooled and the precipitated product washed with ethanol, water, ethanol, and finally n-hexane. Recrystallisation from benzene–n-hexane gave white crystals (0·34 g, 74%), m.p. 160—162° in air, 213—215° sealed under nitrogen (Found: C, 72·4; H, 5·15. Calc. for $C_{54}H_{47}OP_3Ru$: C, 71·95; H, 5·15%).

Method b. Solutions of hydrated ruthenium trichloride (0·13 g, 0·5 mmol) in 2-methoxyethanol (10 ml), aqueous formaldehyde (5 ml, 40% w/v soln.), and potassium hydroxide (0·2 g) in water (5 ml) were added in rapid succession to a solution of triphenylphosphine (0·78 g, 3 mmol) in boiling 2-methoxyethanol (40 ml). The mixture was heated under reflux, cooled to 30°, and the precipitated product washed with ethanol, water, ethanol, and finally n-hexane; it was then dried *in vacuo* to give white crystals (0·34 g, 74%) (Found: C, 71·85; H, 4·8. Calc. for $C_{54}H_{47}OP_3Ru$: C, 71·95; H, 5·15%). Dihydridocarbonyltris(triphenylphosphine)ruthenium was also prepared by Method a, using triethylamine (5 ml) or sodium carbonate (0·2 g) in place of potassium hydroxide; yields were 76 and 72% respectively.

Tricarbonylbis(triphenylphosphine)ruthenium. Solutions of hydrated ruthenium trichloride (0·39 g, 1·5 mmol) in 2-methoxyethanol (30 ml), aqueous formaldehyde (30 ml, 40% w/v soln.), and potassium hydroxide (0·6 g) in 2-methoxyethanol (30 ml) were added in rapid succession to a well stirred boiling solution of triphenylphosphine (2·37 g, 9 mmol) in 2-methoxyethanol (90 ml). The reaction solution was heated under reflux for 1 h and then cooled to room temperature. The resultant pale yellow microcrystalline precipitate was washed with ethanol, water, ethanol, and finally n-hexane; it was then dried *in vacuo* (0·95 g, 89%), m.p. 170—173° in air and 262—266° sealed under nitrogen (Found: C, 66·3; H, 4·5; 4·2; P, 8·85. Calc. for $C_{39}H_{30}O_3P_2Ru$: C, 66·0; H, 4·25; P, 8·75%).

Tricarbonylbis(triphenylphosphine)ruthenium was similarly prepared as pale yellow crystals using triethylamine (15 ml) or sodium carbonate (0·6 g) in place of potassium hydroxide; yields were 65 and 88% respectively.

*Tricarbonylbis(tri-*p*-tolylphosphine)ruthenium.* This complex was similarly prepared using tri-*p*-tolylphosphine and recrystallised from dichloromethane–methanol as white microcrystals (70%); ν(CO) 1890vs cm^{-1}; m.p. 178—181° in air (Found: C, 67·55; H, 5·2; P, 7·45. $C_{45}H_{42}O_3P_2Ru$ requires C, 68·1; H, 5·35; P, 7·8%.

*Tricarbonylbis(tri-*p*-methoxyphenylphosphine)ruthenium.* This complex was similarly prepared using tri-*p*-methoxyphenylphosphine and recrystallised from dichloromethane–methanol as pale yellow microcrystals (50%); ν(CO) 1870, 1890 cm^{-1}; m.p. 152—158° in air (Found: C, 59·8; H, 4·6; P, 6·65. $C_{45}H_{42}O_9P_2Ru$ requires C, 59·55; H, 4·65; P, 6·85%).

Dinitrosylbis(triphenylphosphine)ruthenium. A solution of hydrated ruthenium trichloride (0·26 g, 1·0 mmol) in ethanol (10 ml) was added to a stirred solution of triphenylphosphine (1·56 g, 6·0 mmol) in boiling ethanol (60 ml). Triethylamine (*ca.* 4 ml) was rapidly added until a dark purple colour developed; *N*-methyl-*N*-nitrosotoluene-*p*-sulphonamide (0·4 g) in ethanol (20 ml) and triethylamine (6 ml) were then added immediately. The mixture was heated under reflux for 5 min and then allowed to cool. The precipitate was filtered off, washed successively with ethanol, water, ethanol and n-hexane, and then dried *in vacuo* to give the required product as red microneedles (0·55 g, 82%); ν(NO) 1665 and 1619 cm^{-1}; m.p. 144—145° in air and 185—186° under nitrogen (Found: C, 62·15; H, 4·15; N, 4·05; P, 8·25. Calc. for $C_{36}H_{30}N_2O_8Ru$: C, 63·05; H, 4·4; N, 4·1; P, 9·05%).

Osmium Complexes.—Hydridochlorocarbonyltris(triphenylphosphine)osmium. Solutions of sodium hexachloro-osmate (0·673 g, 1·2 mmol) in 2-methoxyethanol (35 ml), and aqueous formaldehyde (15 ml, 40% w/v soln.) were added in rapid succession to a vigorously stirred, boiling solution of triphenylphosphine (1·97 g, 7·5 mmol) in 2-methoxyethanol (75 ml). The reaction mixture was heated under reflux for 30 min, during which time the colour changed from brown-red to yellow; it was then allowed to cool to room temperature. The precipitated product was washed with ethanol, water, ethanol, and finally n-hexane; it was then dried *in vacuo* to give white microcrystals (1·2 g, 95%), m.p.

179—183° in air, 289—290° sealed under nitrogen (Found: C, 63·55; H, 4·7; P, 8·5. Calc. for $C_{55}H_{46}ClOOsP_3$: C, 63·4; H, 4·45; P, 8·9%).

Dihydridocarbonyltris(triphenylphosphine)osmium. Solutions of sodium hexachloro-osmate (0·84 g, 1·5 mmol) in 2-methoxyethanol (30 ml), aqueous formaldehyde (12 ml, 40% w/v soln.), and potassium hydroxide (0·84 g) in 2-methoxyethanol (15 ml) were added in rapid succession to a vigorously stirred boiling solution of triphenylphosphine (4·72 g, 18 mmol) in 2-methoxyethanol (75 ml). The mixture was heated under reflux for 30 min, during which time the colour changed to pale yellow and a white precipitate separated; it was then allowed to cool to room temperature. The precipitate was washed with ethanol, water, ethanol, and finally n-hexane to give white micro-crystals (1·14 g, 73%), m.p. 202—204° in air, 245—246° under nitrogen (Found: C, 65·85, 65·35; H, 4·65, 5·0; P, 9·5. Calc. for $C_{55}H_{47}OOsP_3$: C, 65·6; H, 4·7; P, 9·25%).

Dihydridodicarbonylbis(triphenylphosphine)osmium. Solutions of sodium hexachloro-osmate (1·18 g, 2·0 mmol) in 2-methoxyethanol (30 ml), aqueous formaldehyde (55 ml, 40% w/v soln.), and potassium hydroxide (2·0 g) in 2-methoxyethanol (20 ml) were added in rapid succession to a vigorously stirred, boiling solution of triphenylphosphine (0·92 g, 3·5 mmol) in 2-methoxyethanol (100 ml). The very dark reaction solution was heated under reflux for 30 min during which time it slowly lightened in colour; it was then allowed to cool to room temperature. The precipitated product was washed with ethanol, water, ethanol, and finally n-hexane and then dried *in vacuo* to give creamy white microcrystals (0·93 g, 57%), m.p. 243—244° in air, 257—258° sealed under nitrogen (Found: C, 59·15; H, 4·5; P, 8·25. Calc. for $C_{38}H_{32}O_2OsP_2$: C, 59·05; H, 4·15; P, 8·0%).

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Spectrophotometric Studies of Alizarin Sulphonate and Ti (III) Complex

S. S. A. RIZVI* & N. AHMAD†

Department of Chemistry, Aligarh Muslim University, Aligarh

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Alizarin sodium sulphonate forms coloured complex with several rare earths viz., Y, La, Pr, Nd, Gd and Eu as reported by Rinchart[1]. The complexes of Th, Na, Mo, Al, Cu and Indium[2-7] have been reported in the literature.

Ti (III), chloride gives a red colour complex with Alizarin sulphonate in aqueous solution. In the present work the complex was not isolated but was studied in solution. The metal ligand ratio was found out by various methods using spectrophotometry.

EXPERIMENTAL

$TiCl_3$ was purified by crystallizing by a method described in Mellor[8]. The crystals were dried up under vacuum and covered with toluene layer, stored in dark and in an inert atmosphere to check oxidation.

The stock solution of $TiCl_3$ was prepared in air free double distilled conductivity water, covered with kerosene oil. This solution was standardised by adding a known volume of it in excess of pure ferric alum solution, containing sulphuric acid and titrating the resulting $FeSo_4$ against the standard $KMno_4$ solution.

Determination of Metal Ligand ratio : Spectronic-20 Bausch and Lomb spectrophotometer was used. Vosburgh and Cooper mothod[9] shows the formation of a single complex and has been further supported by Job's method[10] of continuous variations, slope ratio method[11] and molar ratio method[12].

DISCUSSION

Vosburgh and Cooper method bears the testimony to the formation of a single complex under the usual conditions of colorimetric analysis in aqueous medium and also show that the maximum absorption occurs at 430 mμ, Job's method of continuous variations indicate a molar ratio of 1 : 1 for the metal and the ligand. The ratio is the same for its complex with many trivalent ions as Sc, Y, Al.

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* Address for correspondence—Chemistry Deptt., I.I.T., New Delhi-29.

† Chemistry Department, A.M.U., Aligarh.

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Transition-metal Complexes Containing Phosphorus Ligands. Part IX.[1] Triaryl Phosphite Derivatives of Palladium(II) and Platinum(II) Dihalides

By **Naseer Ahmad, Eric W. Ainscough, Tom A. James,** and **Stephen D. Robinson,*** Department of Chemistry, King's College, Strand, London WC2R 2LS

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An extensive series of triaryl phosphite derivatives of palladium(II) and platinum(II) dihalides, $MX_2[P(OAr)_3]_2$ (M = Pd or Pt, X = Cl, Br, or I, Ar = phenyl, *p*-chlorophenyl, *o*-, *m*-, or *p*-tolyl), have been isolated as air-stable crystalline solids by reacting triaryl phosphites, $P(OAr)_3$ and, where appropriate, lithium halides, LiX, with the salts Na_2MCl_4 in ethanol or the neutral complexes MX_2(cyclo-octa-1,5-diene) in benzene solution. The new complexes have been characterised and their stereochemistry investigated by i.r. and n.m.r. spectroscopy. Palladium derivatives containing bulky tri-*o*-tolyl phosphite or iodide ligands were obtained as *trans*-isomers or *cis–trans* mixtures, the remaining complexes occurred predominantly as the *cis*-isomers. An extensive compilation of ^{31}P n.m.r. data is given.

In furtherance of our studies on the *ortho*-metallation of co-ordinated triaryl phosphite ligands we required to synthesise triaryl phosphite derivatives of palladium(II) and platinum(II) dihalides, $MX_2[P(OAr)_3]_2$. These complexes, unlike their triarylphosphine counterparts, have previously attracted little attention, and few syntheses have been recorded in the literature. One complex, $PtCl_2[P(OPh)_3]_2$, has been studied in some detail [2-5] and a few other examples,[6] including the difluoro-derivative $PtF_2[P(OPh)_3]_2$ [7] have been briefly described, however no general study has previously been reported. We have therefore developed the general syntheses described below for the preparation of the class of compounds $MX_2[P(OAr)_3]_2$ and have characterised the products.

The two methods of synthesis employed are based on simple metathetical exchange reactions. One of these, adapted from an earlier synthesis [2] of $PtCl_2[P(OPh)_3]_2$, involves reaction of triaryl phosphite, sodium tetrachloro-palladite(II) or -platinite(II) and, where appropriate, an excess of lithium bromide or iodide in warm ethanol; the other utilises the facile displacement of cyclo-octa-1,5-diene from the complexes $MX_2(C_8H_{12})$ by triaryl phosphite ligands in benzene solution. The latter method, though generally the most convenient, frequently gave products solvated with benzene; this may be removed by recrystallisation of the solvated complexes from dichloromethane–methanol. Difficulty experienced in crystallising some tritolyl phosphite derivatives from the ethanol reaction solutions (first synthetic route) is reflected in the modest yields recorded in several instances.

All the new triaryl phosphite complexes are air-stable, crystalline, solids with very sharp m.p.s, and are very soluble in chloroform and dichloromethane. They vary in colour from white to dark orange-red depending upon the particular metal and halide present; the intensity of colour increases in the expected sequences Cl < Br < I and Pt < Pd. The *trans*-isomers are darker coloured than the *cis*-isomers and, unlike the latter, are readily soluble in benzene. The stereochemistry of the new triaryl phosphite derivatives was determined by far-i.r. and n.m.r. spectroscopy. The dichloro-derivatives, $MCl_2[P(OAr)_3]_2$ (Ar = phenyl, *m*-tolyl, *p*-tolyl, *p*-chlorophenyl), each show two bands in their i.r. spectra (Table) attributable to *sym* and *asym* vibrations of a *cis*-MCl_2 group and are accordingly assigned as *cis*-

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[7] J. McAvoy, K. C. Moss, and D. W. A. Sharp, *J. Chem. Soc.*, 1965, 1376.

isomers, in agreement with an earlier conclusion [5] concerning the stereochemistry of $PtCl_2[P(OPh)_3]_2$. The appearance of a third band at *ca.* 360—375 cm^{-1} in the spectra of the corresponding tri-*o*-tolyl phosphite derivatives leads to the formulation of these complexes as *cis–trans*-isomer mixtures. These conclusions were confirmed by ^{31}P n.m.r. spectroscopy, each isomer gives rise to a single ^{31}P resonance with a characteristic chemical shift and, where appropriate, ^{195}Pt–^{31}P coupling, thus permitting detection and identification of isomers present. The values of $^1J(^{195}Pt–^{31}P)$ recorded for *cis*- and *trans*-isomers are of similar magnitude to those previously recorded for related systems,[5,8] and show the same dependence on the nature of the halide ligands.[8] In agreement with an earlier report,[9] that in some related tertiary phosphine complexes, $PdX_2(PR_3)_2$ the tendency to adopt a *trans*-configuration is halide dependent and increases in the order Cl ~ Br < I.[9]

EXPERIMENTAL

Sodium chloropalladite was used as purchased, sodium chloroplatinite was obtained by careful evaporation of a 10% aqueous solution (Johnson Matthey) Triphenyl and tri-*p*-tolyl phosphites were used as purchased, other triaryl phosphites were prepared and purified by literature methods [10]

I r spectra (4000—200 cm^{-1}) were recorded on a Perkin-Elmer 621 grating spectrometer using samples mulled in

Analytical, i r ,[a] and ^{31}P n m r [b] data of platinum(II) and palladium(II) derivatives, $MX_2[P(OAr)_3]_2$

						cis			*trans*		
M	X	Aryl (Ar)	C (%) *	H (%) *	Other (%) *	δ	^1J(PtP)	M–Cl	δ	^1J(PtP)	M–Cl
Pt	Cl	Phenyl	48 65 (48 75)	3 5 (3·4)	Cl, 8 25 (8·0)	−59 33	5793	310, 335			
		o Tolyl	52 15 (51·95)	4·45 (4 35)	Cl, 7 0 (7 3)	−57 04	5859	315, 340	−74 86	4405	360
		m Tolyl	51 85 (51·95)	4 25 (4·35)	Cl, 7 6 (7·3)			310, 335			
		p Tolyl	51 6 (51 95)	4 35 (4 35)	Cl, 7 5 (7 3)	−58 71	5840	310, 330			
		p Chlorophenyl [c]	42 7 (43 05)	2 6 (2 6)		−61 29	5746	310, 335			
	Br	Phenyl	44 8 (44 35)	3 2 (3 1)	Br, 16 0 (16 35)	−59 17	5728				
		o Tolyl	47 9 (47 6)	4 0 (4 0)	Br, 15 65 (15 1)	−57 44	5840				
		m Tolyl	47 85 (47 6)	4 1 (4 0)	P, 6 1 (5 85)						
		p Tolyl	47 65 (47 6)	4 0 (4 0)	Br, 14 95 (15 1)	−59 33	*d*				
		p Chlorophenyl	36 65 (36 55)	2 05 (2 05)	P, 5 2 (5 25)	−61 13	5668				
		Phenyl	40 6 (40 45)	3 0 (2 85)	I, 23 5 (23 75)	−59 2	5600				
		o-Tolyl	43 85 (43 75)	3 75 (3 65)	I, 21 55 (22 0)	−57 86	5602				
		m Tolyl	43 6 (43 75)	3 9 (3 65)	I, 22 35 (22 0) [e]	−58 24	5650				
		p-Tolyl	43 45 (43 75)	3 75 (3 65)	I, 22 3 (22 0)	−59 49	5519				
		p Chlorophenyl	34 15 (33 85)	2 1 (1 9)	P, 5 15 (4 85)	−60 8	5442				
Pd	Cl	Phenyl	54 15 (54 2)	3 85 (3 8)	Cl, 8 65 (8 9)	−83·42		300, 335—340			
		o Tolyl	56 9 (57 2)	4 8 (4 8)	Cl, 8 3 (8 05) [f]	−84 88		300, 335	−86 81		375
		m Tolyl	57 45 (57 2)	4 85 (4 8)	Cl, 7 95 (8 05)			310, 335			
		p Tolyl	57 0 (57 2)	4 6 (4 8)	Cl, 7 9 (8 05)	−83 52		310, 335			
		p Chlorophenyl [c]	45 90 (46 6)	2 95 (2 8)	Cl, 25 65 (26 2)	−84 66		308, 327			
	Br	Phenyl	49 1 (48 75)	3 55 (3 4)	Br, 18 45 (18 0)	−82 37					
		o Tolyl	51 7 (51 95)	4 3 (4 35)		−84 7			−90 3		
		m Tolyl	51 75 (51 95)	4 5 (4 35)	Br, 17 0 (16 45) [g]	−81 55					
		p Tolyl	51 75 (51 95)	4 5 (4 35)		−82 86					
		p Chlorophenyl	39 6 (39 55)	2 15 (2 2)	P, 5 45 (5 65)	−83 52			−87 44		
		Phenyl	44 0 (44 1)	3 3 (3 1)	P, 6 1 (6 3)	−82 24			−93 6		
		o Tolyl	47 8 (47 35)	4 05 (4 0)	P, 5 4 (5 8)				−92 7		
		m Tolyl	47 5 (47 35)	4 3 (4 0)	P, 6 0 (5 8)	−81 36			−92 7		
		p Tolyl	46 9 (47 35)	3 85 (4 0)	P, 6 1 (5 8)	−82 87			−93 68		
		p-Chlorophenyl	36 65 (36 4)	2 25 (2 0)	P, 5 5 (5 2)				−95 12		

[a] I r spectra recorded from Nujol mulls [b] P N m r spectra recorded at 36 43 MHz in deuteriochloroform solution with field-frequency lock provided by deuteriochloroform Chemical shifts (±0 2 p p m) are given relative to 85% H_3PO_4, J values ±2 Hz [c] Benzene adducts $MCl_2[P(OC_6H_4Cl)_3]_2{\cdot}C_6H_6$ [d] Resolution insufficient to permit accurate measurement of ^1J(PtP) [e] P, 5 65 (5 35)% [f] P, 6 9 (7 0)% [g] P, 6·05 (6 4)%
* Calculated values in parentheses

Occurrence of appreciable concentrations of *trans*-isomers in the tri-*o*-tolyl phosphite derivatives may be attributed to steric factors arising from the bulky nature of this particular ligand We were unable to assign the rather complex far-i r spectra obtained for the bromo- and iodo-derivatives, and therefore base our stereochemical assignments for these products on ^{31}P n.m.r data alone These indicate that the complexes are predominantly *cis*, except for the palladium derivatives containing bulky tri-*o*-tolyl phosphite and/or iodide ligands which occur as *trans*-isomers or *cis–trans* mixtures. Confirmation of stereochemical assignments for the tritolyl phosphite derivatives was provided by ^1H n m r data. Pure isomers give rise to single resonances (*ca* τ 7·6—7·9, *o*-tolyl, *ca* τ 8·0—8·15, *m*- or *p*-tolyl) attributable to the methyl protons of the tolyl groups, *cis–trans*-isomer mixtures give rise to two singlets of differing intensity in the same region Our stereochemical assignments for the palladium derivatives are

[8] A Pidcock, R E Richards, and L M Venanzi, *J Chem Soc* (*A*), 1966 1707

Nujol ^1H N m r spectra were measured in deuteriobenzene with T M S as internal reference using a Varian HA 100 spectrometer Phosphorus-31 n m r. spectra were recorded in deuteriochloroform using a Bruker HFX 90 spectrometer and Fourier transform accessory M p s (corrected) were taken on a Kofler hot-stage apparatus Microanalyses by Dr Strauss, Oxford

Dichlorobis(triphenyl phosphite)platinum(II) —Cold solutions of triphenyl phosphite (0·62 g, 0·002 mol) in ethanol (4 ml) and sodium tetrachloroplatinite tetrahydrate (0·4 g, 0 001 mol) in ethanol (8 ml) were mixed The mixture was gently warmed for 30 s, shaken at room temperature for 10 min, then cooled at 0°, after 30 min the colourless precipitate was filtered off, washed with ethanol, 50% aqueous ethanol, ethanol, and n-hexane, then dried *in vacuo* to give the required product (0·7 g, 80%) Recrystallisation from dichloromethane–methanol gave white crystals (m p 187—189°)

Similarly prepared using the appropriate triaryl phosphites were *dichlorobis(tri-o-tolyl phosphite)platinum*(II) as

[9] J M Jenkins and B L Shaw, *J Chem Soc* (*A*) 1966, 770
[10] G M Kosolapoff, ' Organophosphorus Compounds Wiley, New York 1950, pp 180—210

white microprisms, yield 80%, m p 195—196°, *dichlorobis(tri-m-tolyl phosphite)platinum*(II) as white microneedles, yield 75%, m.p 151—152°, *dichlorobis(tri-p-tolyl phosphite)platinum*(II) as white microcrystals, yield 75%, m p 182—184°

Dichlorobis(tri-p-chlorophenyl phosphite)platinum(II) — Tri-*p*-chlorophenyl phosphite (0·82 g, 0·002 mol) was added to a suspension of $PtCl_2(C_8H_{12})$ (0·37 g, 0·001 mol) (C_8H_{12} = cyclo-octa-1,5-diene) in benzene (8 ml) After gentle warming for a few minutes the mixture was filtered, diluted with *n*-hexane, cooled at 0° for 30 min, then allowed to stand at room temperature until crystallisation was complete The resultant white precipitate was filtered off, washed with n-hexane, and dried *in vacuo* as a benzene solvate, $PtCl_2[P(OC_6H_4Cl)_3]_2.C_6H_6$ Yield 0·8 g, 73% Recrystallisation from dichloromethane–methanol gave white crystals of solvent-free product (m p 195—196°)

Dibromobis(triphenyl phosphite)platinum(II) —Solutions of lithium bromide (1 42 g) in ethanol (10 ml) and triphenyl phosphite (0 62 g, 0 002 mol) in ethanol (4 ml) were added to a cold solution of sodium tetrachloroplatinite tetrahydrate (0 4 g, 0 001 mol) in ethanol (8 ml) The mixture was warmed gently for *ca* 30 s, shaken at room temperature for 10 min, then cooled at 0° for 45 min The resultant precipitate was filtered off, washed successively with ethanol, 50% aqueous ethanol, ethanol, and n-hexane, then dried *in vacuo* Yield 0 53 g, 50% Recrystallisation from dichloromethane–methanol gave white microprisms (m p 187—188°)

Similarly prepared using the appropriate triaryl phosphite and lithium halide were *dibromobis(tri-o-tolyl phosphite)platinum*(II) as white microcrystals, yield 55%, m p 194—195°, *dibromobis(tri-m-tolyl phosphite)platinum*(II) as white microprisms, yield 50%, m p 173—174°, *dibromobis(tri-p-tolyl phosphite)platinum*(II) as white microneedles, yield 50%, m p 209—210°, *di-iodobis(triphenyl phosphite)platinum*(II) as yellow microprisms, yield 60%, m p 185—187°, *di-iodobis(tri-o-tolyl phosphite)platinum*(II) as yellow microcrystals, yield 60%, m p 170—171°, *di-iodobis(tri-m-tolyl phosphite)platinum*(II) as yellow microprisms, yield 10%, m p 168—169° The following were prepared from the appropriate cyclo-octa-1,5-diene complex $PtX_2(C_8H_{12})$ as described above *dibromobis(tri-p-chlorophenyl phosphite)platinum*(II) as white flaky crystals, yield 77%, m p 189—190°, *di-iodobis(tri-p-chlorophenyl phosphite)platinum*(II) as canary-yellow crystals, yield 78%, m p. 174°; *di-iodobis(tri-p-tolyl phosphite)platinum*(II) as canary-yellow crystals, yield 58%, m p 185—186°

The palladium complexes were prepared from sodium tetrachloropalladite tetrahydrate or, where stated, from dihalogeno(cyclo-octa-1,5-diene)palladium by methods similar to those employed to synthesise their platinum analogues Palladium derivatives isolated and characterised were *dichlorobis(triphenyl phosphite)palladium*(II) as white microcrystals, yield 85%, m p 175—180°, *dichlorobis(tri-o-tolyl phosphite)palladium*(II) as white microcrystals, yield 80%, m p 171—174°, *dichlorobis(tri-m-tolyl phosphite)palladium*(II) as white microcrystals, yield 80%, m p 147—148°, *dichlorobis(tri-p-tolyl phosphite)palladium*(II) as white microprisms, yield 80%, m p 179°, *dichlorobis(tri-p-chlorophenyl phosphite)palladium*(II) from dichloro(cyclo-octa-1,5-diene)-palladium as benzene solvated white microprisms, yield 80%, m p 154—155°, *dibromobis(triphenyl phosphite)-palladium*(II) as yellow microplates, yield 80%, m p 176—178°, *dibromobis(tri-o-tolyl phosphite)palladium*(II) as orange-red microcrystals, yield 75%, m p 152—153° *dibromobis(tri-m-tolyl phosphite)palladium*(II) as yellow microneedles, yield 70%, m p 162—163°, *dibromobis(tri-p-tolyl phosphite)palladium*(II) as yellow microneedles, yield 70%, m p 161—162°, *dibromobis(tri-p-chlorophenyl phosphite)palladium*(II) from dibromo(cyclo-octa-1,5-diene)-palladium as yellow-orange flaky crystals, yield 78%, m p 212—214°, *di-iodobis(triphenyl phosphite)palladium*(II) as dark orange microprisms, yield 50%, m p 189—191°, *di-iodobis(tri-o-tolyl phosphite)palladium*(II) as red microprisms, yield 50%, m p 164—165°, *di-iodobis(tri-m-tolyl phosphite)palladium*(II) as dark red prismatic needles, yield 30%, m p 129—130°, *di-iodobis(tri-p-tolyl phosphite)-palladium*(II) as orange microcrystals, yield 50% m p 204—205°, *di-iodobis(tri-p-chlorophenyl phosphite)-palladium*(II) from di-iodo(cyclo-octa-1,5-diene)palladium as orange-red flaky crystals, yield 72%, m p 198—199°

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Transition-metal Complexes Containing Phosphorus Ligands. Part X.[1] *ortho*-Metallation Reactions Involving Some Triaryl Phosphite Derivatives of Palladium(II) and Platinum(II) Dihalides

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Triaryl phosphite complexes of palladium(II) and platinum(II), $MX_2[P(OAr)_3]_2$ (M = Pd or Pt X = Cl, Br, or I, Ar = phenyl, *p*-chlorophenyl, *o*-, *m*-, or *p*-tolyl), react in boiling decalin, with elimination of a molecule of hydrogen halide, HX, to afford *ortho*-metallated triaryl phosphite derivatives The tendency to undergo metallation is dependent upon the anionic ligands present and increases I < Br < Cl The structures and stereochemistry of these products have been determined by i.r. and n.m r. spectroscopy Treatment of the *ortho*-metallated complexes with hydrogen halide in dichloromethane leads to rapid reversal of the *ortho*-palladation reactions and slow reversal of the *ortho*-platination reactions. Mechanistic aspects of the *ortho*-metallation processes are discussed

As part of our continuing investigation of trialkyl and triaryl phosphite complexes of the platinum metals, we now report our results on the *ortho*-metallation reactions of palladium(II) and platinum(II) triaryl phosphite derivatives. Part of the work described in this paper has been discussed previously in a preliminary communication.[2] Similar studies of ruthenium[3] and iridium[4] triaryl phosphite complexes were reported in previous papers; related investigations involving triaryl phosphite derivatives of the other platinum group metals are in progress, and will be reported elsewhere.[5]

The extensive occurrence of intramolecular *ortho*-metallation reactions, involving activation and cleavage of *ortho*-carbon–hydrogen bonds in aromatic nitrogen and phosphorus donor ligands co-ordinated to transition-metal ions, is now well established, and the substantial body of work published in this field has recently been reviewed.[6,7] Intramolecular metallation reactions, including *ortho*-metallations, show a very strong tendency to form five-membered chelate rings,[6] this behaviour is clearly demonstrated in the reactions of the amines, $Ph(CH_2)_nNMe_2$ (n = 0—3), with palladium halides. *NN*-Dimethylbenzylamine alone undergoes metallation, forming a product with a five-membered chelate ring, the other amines all yield simple amine complexes, $PdCl_2[Me_2N(CH_2)_nPh]_2$.[8] Intramolecular *ortho*-metallation of co-ordinated triaryl phosphites affords sterically favoured, five-membered chelate rings; it is therefore not surprising that these ligands undergo metallation relatively readily. Examples of *ortho*-metallation reactions involving triaryl phosphite ligands co-ordinated to ruthenium,[3,9-11] osmium,[5] rhodium,[10] iridium,[4,12,13] palladium,[2] and platinum[2] have now been observed. In addition, exchange of *ortho*-aromatic hydrogen and deuterium provides evidence for the reversible *ortho*-metallation process:

$$CoH[P(OPh)_3]_4 \rightleftharpoons Co[P(OC_6H_4)(OPh)_2][P(OPh)_3]_3 + H_2$$

In this system however the equilibrium lies far to the left and no *ortho*-metallated product has been isolated.[10]

Much of the early work on *ortho*-metallation reactions involved complexes of palladium(II) and platinum(II) containing aromatic nitrogen donor ligands,[6] and interest in these systems has been sustained.[14-16] More recently, the facile metallation of aryl groups in sterically crowded palladium(II) and platinum(II) derivatives containing bulky tertiary phosphine ligands has been reported.[17-19] Palladation and platination reactions involving intramolecular attack on the *o*-methyl groups of co-ordinated *o*-tolylphosphines[17-19] or the terminal methyl groups of triethyl-[20] and *t*-butyl-n-propylphosphines[17] have also been described. Prior to the present work, no examples of palladation or platination reactions involving tertiary phosphite ligands had been reported.

We now find that the palladium(II) and platinum(II) triaryl phosphite derivatives,[1] $MX_2[P(OAr)_3]_2$ (M = Pd or Pt, X = Cl, Br, [I], Ar = phenyl, *p*-chlorophenyl, *o*-, *m*-, or *p*-tolyl),† react in boiling decalin with loss of hydrogen halide, HX, to afford air-stable, white, crystalline complexes. These products are formulated

† For discussion of stereochemistry of these complexes see preceding paper

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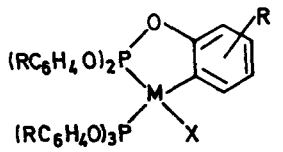
[19] A J Cheney and B L Shaw, *J C S Dalton*, 1972, 860
[20] S Bresadola, P Rigo, and A Turco, *Chem Comm*, 1968, 1205

(see below) as metal-*ortho* carbon bonded derivatives of palladium(II) and platinum(II) (I) In accord with previous usage [4] phosphite ligands are designated (P) and the chelate ligands derived from them by metallation are represented by (P–C) The structure (I) is therefore abbreviated to MX(P–C)P in the text



(I)

(M = Pd or Pt X = Cl Br or [I] R = H, Cl or Me)

The gaseous hydrogen halide, 1 mol per mol of reacted complex, liberated during these reactions was collected and estimated as silver halide The rate of metallation decreases in the sequence Cl > Br > I and Pt > Pd for a given phosphite ligand, thus the platinum dichloride complexes, $PtCl_2[P(OAr)_3]_2$, react to completion in 2 h while the platinum and, in particular, palladium di-iodo derivatives $MI_2[P(OAr)_3]_2$ afford only traces of desired product after reaction times of 4—6 h Prolonged reactions (2—4 days) of the platinum complexes, $PtI_2[P(OAr)_3]_2$ in boiling decalin lead to evolution of hydrogen iodide (*ca* 0 6 mol per mol of complex) and formation of an intractable white solid residue However attempts to isolate and crystallise the desired metallated complexes from these reaction products were unsuccessful The palladium complexes, $PdX_2[P(OAr)_3]_2$, undergo some decomposition in boiling decalin, thus their *ortho*-metallation reactions are accompanied by deposition of palladium metal These metallation reactions are not suited to kinetic study and no attempt has been made to establish a relationship between reaction rate and the structure of the triaryl phosphite ligands Our qualitative observations concerning the rates of *ortho* metallation are discussed further in the section on mechanism (see below) Attempts to form di-metallated products $M(P–C)_2$, by boiling the metallated complexes, MCl(P–C)P, in decalin for periods of 2—3 days were unsuccessful

The *ortho*-palladated compounds PdCl(P–C)P (P = triphenyl or tri *o*-tolyl phosphite) react rapidly with hydrogen chloride in cold dichloromethane to regenerate the parent dichloride complexes, similar reactions involving the *ortho*-platinated species, PtCl(P–C)P, proceed slowly over a period of 24 h Cleavage of platinum–carbon bonds by hydrogen chloride has previously been observed to occur with the non-chelated complexes *cis*- and *trans*-$PtRCl(PR'_3)_2$ (R = alkyl or aryl) [21,22] and with the chelate species PtCl[CH(Me)-$C_6H_4PPh_2$][PPh_2(*o*-vinylphenyl)] [23] However, Cheney *et al* were unable to cleave the platinum–carbon bonds in their mono-metallated tertiary phosphine derivatives, and tentatively attributed the inert character of these complexes to steric factors and/or the stability of the chelate ring [17,18] The relatively facile de-platination of the bulky co-ordinated tri-*o*-tolyl phosphite ligands, observed in the present work, is perhaps rather surprising in view of the conclusions of Cheney *et al* that steric congestion is important in promoting metallation within these systems [17 19]

Attempts to isolate *ortho*-metallated products from the reaction of the platinum(0) complex, $Pt[P(OPh)_3]_4$ in boiling decalin were inconclusive, the intractable reaction product showed i r evidence for the presence of small quantities of metallated material but none could be isolated

The new complexes, isolated from the reactions of the dihalide derivatives, $MX_2[P(OAr)_3]_2$, in boiling decalin, are formulated as the metal *ortho*-carbon bonded species (I) on the basis of the evidence described below The presence of the *ortho*-metallated chelate ligands (P–C) was established by the appearance of characteristic i r bands [3] at 1100, 900, and 800 cm^{-1} (P = triphenyl phosphite) and at 1120, 900, and 750 cm^{-1} (P = tri-*p*-tolyl phosphite) The i r spectra of the *ortho*-metallated products obtained from the palladium(II) and platinum (II) derivatives of tri-*o*-tolyl, tri-*m*-tolyl, and tri-*p*-chlorophenyl phosphites show similar characteristic bands, these are listed in Table 1 The band at 1120

TABLE 1

Infrared data [a] for metallated complexes MX(P–C)P bands [b] associated with metallated ligands

Triphenyl phosphite	*ca 1105*m 1030m *900*m *800*m
Tri *o* tolyl phosphite	1395w 1250w *1063*w *ca 835*m *775*m
Tri *m* tolyl phosphite	*1030*m *810*m *740*m
Tri *p* tolyl phosphite	*1120*w *900*m *850*w *ca 755*m, 662m
Tri *p* chlorophenyl phosphite	1115vw *1030*m 905m *780*m *709*m

[a] Recorded from Nujol mulls in cm^{-1} [b] Diagnostically most useful bands in italic

cm^{-1} characteristic of *o*-metallated tri-*p*-tolyl phosphite is often of low intensity, [3] we find that the presence of this chelate group is more convincingly diagnosed by the appearance of a strong band at 900 cm^{-1} ^{1}H N m r spectra of the parent tri-*o*-tolyl, tri-*m*-tolyl, and tri-*p*-tolyl phosphite complexes, *cis*- or *trans*-$MX_2[P(OC_6H_4Me)_3]_2$ each show a single sharp resonance at τ *ca* 7 6—8 2, attributable to six equivalent methyl groups [1] However, integrated n m r spectra of the *ortho*-metallated products derived from these tritolyl phosphite complexes each show three bands of relative intensity 1 2 3 at τ *ca* 7 6—8 2 attributable to a total of six methyl groups in three different chemical environments (a, b, c) (II, Table 2)

None of these spectra provides any evidence for the presence of metallated methylene groups, we therefore conclude that the intramolecular metallation reactions occur at an *ortho* aromatic site in each complex The structure of the products derived from the tri-*o* tolyl phosphite complexes, $MX_2[P(OC_6H_4Me)_3]_2$ is particularly interesting Intramolecular metallation of *ortho*-tolyl

[21] J D Ruddick and B L Shaw *J Chem Soc* (*A*) 1969 2801 2964

[22] J Chatt and B L Shaw *J Chem Soc* (*A*) 1959 705 4020

[23] P R Brookes and R S Nyholm *Chem Comm* 1970 169

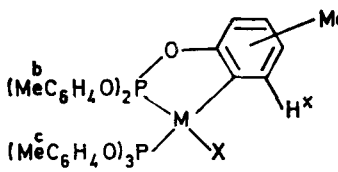
groups in co-ordinated *ortho*-tolylphosphines [17-19,24] and tri-*o*-tolyl phosphite [2] have now been shown to occur at the *ortho*-methyl and *ortho*-aromatic sites respectively to afford products containing five-membered chelate rings.

TABLE 2

^{1}H n.m r.[a] and far-i.r [b] data for *ortho*-metallated complexes, MX(P–C)P

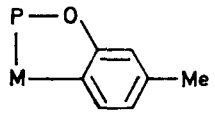
M	X	Phosphite	τ(tolyl-Me) a	b	c	ν(M–Cl)
Pd	Cl	Triphenyl				325
Pd	Cl	Tri-*o*-tolyl	7·80	7·88	8·02	335
Pd	Br	Tri-*o*-tolyl	7·76	7·88	8·00	
Pd	Cl	Tri-*m*-tolyl	8·06	8·12	8·03	320
Pd	Cl	Tri-*p*-tolyl	8·07	8·11	7·96	315
Pt	Cl	Triphenyl				330
Pt	Cl	Tri-*p*-chlorophenyl				310
Pt	Cl	Tri-*o*-tolyl	7·79	7·85	7·96	310
Pt	Br	Tri-*o*-tolyl	7·78	7·86	7·98	
Pt	Cl	Tri-*m*-tolyl	8·08	8·13	8·02	310
Pt	Cl	Tri-*p*-tolyl	8·05	8·09	7·93	310
Pt	Br	Tri-*p*-tolyl	8·06	8·10	7·92	

[a] N m.r spectra recorded at 100 MHz in deuteriobenzene solution, spectra taken in deuteriochloroform show different ordering of the methyl resonances All spectra show complex resonance patterns (*ca* τ 2·3—3·5) arising from aryl protons [b] Far-i r.spectra recorded from Nujol mulls

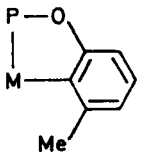


(II)

No evidence for the formation of four- or six-membered chelate rings by metallation of these ligands at the typical of aryl protons *ortho* to a metal–carbon bond and deshielded by the magnetic anisotropy associated with this bond.[25] We assign this resonance to the unique proton, H^x (II), present in the *ortho*-metallated products. The fine structure may be attributed to coupling of this *ortho*-proton with adjacent ring protons, the *trans*-phosphorus nucleus (see below) and, in the platinum complexes, the ^{195}Pt nucleus. Similar low-field resonances have been attributed to protons *ortho* to the metal–ligand bond in metallated derivatives of azobenzene [26] and 8-methylquinoline.[15] The presence of this low-field resonance pattern in the ^{1}H n.m.r. spectra of the metallated tri-*m*-tolyl phosphite complexes permits positive assignment of the sterically favoured structure (IIIa) rather than the alternative (IIIb) for the *ortho*-metallated *m*-tolyl group. In contrast Cheney *et al.* report [17] that the proton *ortho* to the platinum–carbon bond in PtBr(P′–C)P′ [P′ = P(*p*-tolyl)$_2$Bu^t] resonates at *higher* field (τ 4·35) than the other aryl protons present. This anomalous chemical shift may arise from the position, relative to the metal atom, imposed on the *ortho* proton by the highly strained, four-membered chelate ring structure.



(IIIa)



(IIIb)

The stereochemistry about the metal centre in the

TABLE 3

^{31}P N m r [a] data for *ortho*-metallated triaryl phosphite complexes of palladium and platinum, *cis*-MX(P–C)P

M	X	Phosphite	Unmetallated phosphite (P) δ	^1J(Pt–P)	^4J(P–H)	Metallated phosphite (P–C) δ	^1J(Pt–P)	^2J(P–P)
Pd	Cl	Triphenyl	−109·4		13·0	−128·1		56·0
Pd	Cl	Tri-*o*-tolyl	−109·1		12·0	−126·8		54·0
Pd	Cl	Tri-*p*-tolyl	−109·6		12·0	−128·2		52·0
Pt	Cl	Triphenyl	−112·8	3229	12·0	−100·5	6371	29·0
Pt	Cl	Tri-*o*-tolyl	−112·7	3201	12·0	−99·6	6409	30·0
Pt	Cl	Tri-*p*-tolyl	−112·9	3214	12·0	−100·4	6407	30·0
Pt	Br	Tri-*o*-tolyl	−112·0	3200	12·0	−96·5	6371	30·0

[a] Spectra recorded at 36·43 MHz in deuteriochloroform solution with field–frequency lock provided by deuteriochloroform. Chemical shifts are given relative to 85% H_3PO_4 (±0·2 p p.m); *J*-values are ±2 Hz.

alternative sites has been observed to date. It appears therefore, that the electronic features of those carbon–hydrogen bonds available for attack are subordinate to steric factors in directing the course of intramolecular metallation reactions.

The ^{1}H n.m.r. spectra of the *ortho*-metallated complexes all contain a well-resolved multiplet pattern, total intensity 1·0, centred at *ca.* τ 1·0—1·5. This resonance, which is absent from the spectra of the non-metallated parent complexes, lies on the low-field side of other aromatic proton resonances; its τ value is *ortho*-metallated products, MX(P–C)P, has been elucidated by ^{31}P n.m.r. spectroscopy. The first-order spectrum observed for each of these complexes comprises a pair of doublets indicative of coupling ^2J(P–P) between two non-equivalent ^{31}P nuclei. The magnitudes of the coupling constants, ^2J(P–P) (Table 3) are consistent with coupling between mutually *cis*-phosphorus ligands [27] and thus establish the *cis*-stereochemistry previously suggested for these metallated products. In each spectrum the doublet arising from the phosphorus

[24] R Mason and A D C Towl, *J. Chem Soc.* (*A*), 1970, 1601.
[25] A Baici, A Camus, and G. Pellizer, *J. Organometallic Chem*, 1971, **28**, 431 and references therein.
[26] M. I. Bruce, M Z. Iqbal, and F. G A Stone, *J. Chem. Soc.* (*A*), 1970, 3204.
[27] F. H. Allen, A Pidcock, and C R Waterhouse, *J. Chem. Soc.* (*A*), 1970, 2087.

nucleus of the non-metallated phosphite is further split by coupling ^4J(P–H) with the *ortho* proton, H^x, of the metallated aryl group situated in the *trans*-position (II). Broad band proton decoupling experiments confirm that this splitting originates from a phosphorus–hydrogen coupling interaction. The occurrence of the coupling ^4J(P–H) has been observed in the ^{1}H n.m.r. spectra of the metallated aryl group (see above); its appearance in the ^{31}P spectra permits unambiguous assignment of ^{31}P resonances for the metallated and unmetallated phosphite ligands (Table 3). The ^{31}P n.m.r. data recorded for our metallated triaryl phosphite complexes are compatible with those previously reported for similar palladium(II) and platinum(II) triaryl phosphite derivatives.[27] The ' δ ' values (*ca.* −110 p.p.m.) recorded for the unmetallated phosphite ligands are virtually independent of the central metal atom, M; those of the metallated phosphite ligands occur at *ca.* −127 p.p.m. (M = Pd) and at *ca.* −100 p.p.m. (M = Pt). In each of the platinated complexes the phosphorus nucleus *trans* to the halide resonates at higher field and has larger coupling constant ^1J(Pt–P) than that *trans* to the aryl group. The coupling constants ^2J(P–P) are dependent upon the central metal ion, M, and decrease in the order Pd > Pt; a similar trend has recently been observed for the complexes *trans*-$MX_2(PBu_3)[P(OPh)_3]$ and $MCl[(PhO)_2PO][PhO)_2POH](PR_3)$.[27]

The far-i.r. spectra of our metallated complexes, MCl(P–C)P each show a medium intensity band *ca.* 310—325 cm^{-1} attributable to ν(M–Cl); these values are typical of chlorine *trans* to phosphorus in square-planar palladium and platinum complexes, and thus confirm the *cis*-stereochemistry. Many of the corresponding bromo-derivatives, MBr(P–C)P, were not isolated in sufficient quantity for ^{31}P n.m.r. spectroscopy, and their far-i.r. spectra could not be interpreted with confidence, we have therefore been able to establish *cis*-stereochemistry for only one of these products.

The *cis*-configuration observed for our *ortho*-metallated triaryl phosphite derivatives contrasts with the *trans*-configuration reported by Cheney *et al.* for their related products derived from tertiary phosphine platinum(II) dihalide complexes.[18,19] This difference confirms the strong tendency [1] for triaryl phosphite ligands to adopt mutually *cis*-positions in their square planar palladium(II) and platinum(II) derivatives.

Mechanism of ortho-*Metallation*.—The recent literature contains numerous examples of intramolecular metallation reactions involving co-ordinated, aromatic nitrogen or phosphorus donor ligands; however very little positive information has been reported, concerning the mechanisms of these reactions. Tentative mechanisms advanced to date invoke electrophilic attack by the metal on the aromatic ring, and/or oxidative addition of the carbon–hydrogen bond across the metal centre. We tentatively suggest that the *ortho*-metallation processes described in the present paper are initiated by electrophilic attack on the aromatic ring by the metal atom, and may proceed by an oxidative addition and reductive elimination sequence similar to those proposed by Hodges *et al.*[28,29] for their platinum catalysed benzene and alkane deuteriation reactions.

Substituent effects found in the kinetics of metallation of azobenzenes[30] and triarylphosphines[31] suggest that electrophilic attack by the central metal ion on the aromatic ring is the rate-determining step in these particular reactions. In the present study the conditions required to induce metallation deterred us from measuring accurately the relationship between the rate of metallation and the nature or position of substituents on the metallated ring. However, observations that the rates of reaction in our metallation processes and in the isotope exchange reactions of Hodges *et al.*[32] are dependent upon the nature of the co-ordinated halide, and decrease in the sequence Cl > Br > I, support our suggestion that a common rate-determining step, involving electrophilic attack on the hydrocarbon moiety, is operative in both systems. In contrast, Cheney *et al.*[17] report that the rate of metallation of bulky tertiary phosphines, L, in the platinum(II) halide complexes PtX_2L_2 *increases* in the sequence Cl < Br < I; this order, which is the reverse of that discussed above, is consistent with a rate determining step involving oxidative addition across the metal atom. However, stereochemical factors, which are considered to be of prime importance in the complexes studied by Cheney *et al.*,[17-19] also predict the observed order of halide dependence. Finally, in the present study and in the work of Cheney *et al.*,[17-19] on the metallation of tertiary phosphine ligands, the tendency to undergo metallation depends upon the identity of the central metal ion and decreases in the order Pt > Pd. However, other workers report that co-ordinated tertiary amines[8] or azobenzenes[33] undergo palladation more readily than platination. We note these very intriguing differences in behaviour; however, in the absence of detailed kinetic data we prefer not to speculate further concerning their interpretation.

EXPERIMENTAL

Palladium(II) and platinum(II) triaryl phosphite complexes, $MX_2[P(OAr)_3]_2$, were prepared as previously described.[1] Laboratory grade solvents were used as purchased. All reactions were performed under a nitrogen atmosphere.

I.r. spectra (4000—200 cm^{-1}) were recorded on a Perkin-Elmer 621 grating spectrometer using samples mulled in Nujol. ^{1}H N.m.r. spectra were measured in deuteriobenzene with T.M.S. as internal reference, using a Varian

[28] R. J. Hodges, D. E. Webster, and P. B. Wells, *J. Chem. Soc.* (*A*), 1971, 3230.
[29] R. J. Hodges and J. L. Garnett, *J. Phys. Chem.*, 1968, **72**, 1673; 1969, **73**, 1525.
[30] H. Takahashi and J. Tsuji, *J. Organometallic Chem.*, 1967, **10**, 511.
[31] M. A. Bennett and D. L. Milner, *J. Amer. Chem. Soc.*, 1969, **91**, 6983.
[32] R. J. Hodges, D. E. Webster, and P. B. Wells, personal communication.
[33] A. C. Cope and R. W. Siekman, *J. Amer. Chem. Soc.*, 1965, **87**, 3272.

HA100 spectrometer, phosphorus-31 n m r spectra were recorded in deuteriochloroform using a Bruker HFX90 spectrometer and Fourier transform accessory M p s (corrected) were taken on a Kofler hot-stage apparatus Microanalyses by Dr Strauss, Oxford Molecular weight data were recorded on a Hitachi–Perkin-Elmer osmometer using benzene solutions at 43° Evolved hydrogen halides were collected in acidified silver nitrate solution and estimated gravimetrically as silver halide

Platination Reactions

Chloro[triphenyl phosphito(2C,P)](triphenyl phosphite)-platinum(II) $PtCl[(PhO)_2P(OC_6H_4)][P(OPh)_3]$ —Dichlorobis-(triphenyl phosphite)platinum (0 3 g) was heated under reflux in decalin (4—6 ml) for 3 h Hydrogen chloride (*ca* 1 mol) was evolved during the reaction The reaction solution was cooled overnight at room temperature and the resultant precipitate filtered off then washed successively with *n*-hexane, water, ethanol, and *n*-hexane to give the required product (0 22 g, 80%) Recrystallisation from dichloromethane–methanol gave white microcrystals (m p 160°) (Found C, 50 75 H 3 35, P 7 6, Cl, 4·1%, *M*, 905 $C_{36}H_{29}ClO_6P_2Pt$ requires C, 50·85, H, 3 45, P 7 3, Cl, 4 15%, *M*, 850)

The following were similarly prepared from the appropriate triaryl phosphite complexes *Chloro[tri-o-tolyl phosphito(2C,P)](tri-o-tolyl phosphite)platinum*(II) as white microneedles, 80%, m p 195—196° (Found C, 54 15 H, 4 5, P, 6 7, Cl, 4 05 $C_{42}H_{41}ClO_6P_2Pt$ requires C, 54 0 H, 4 4, P, 6 65 Cl, 3 8%) *Chloro[tri-m-tolyl phosphito-(2C,P)](tri-m-tolyl phosphite)platinum*(II) as white microcrystals, 80% (Found C, 53 85, H, 4 6, P, 6 85 Cl, 4 05 $C_{42}H_{41}ClO_6P_2Pt$ requires C, 54 0, H, 4 4 P 6 65 Cl, 3 8%) *Chloro[tri-p-tolyl phosphito(2C,P)](tri-p-tolyl phosphite)platinum*(II) as a white powder, 80% This product was not crystallised (Found C, 54 15, H, 4 65 P, 7 0 Cl, 4 05 $C_{42}H_{41}ClO_6P_2Pt$ requires C, 54 0, H 4 4, P, 6 65, Cl 3 8%) *Chloro[tri-p-chlorophenyl phosphito-(2C,P)](tri-p-chlorophenyl phosphite)platinum*(II) as white microneedles, 85%, m p 174—175° (Found C, 41 2, H, 2 4, P, 5 95, Cl, 23 4%, *M*, 1031 $C_{36}H_{23}Cl_7O_6P_2Pt$ requires C, 40 9, H, 2 2 P, 5 85, Cl, 23 5, *M* 1056) *Bromo[triphenyl phosphito(2C P)](triphenyl phosphite)-platinum*(II) as a white microcrystalline powder, 55% m p 155—170° (Found C 48 45, H, 3 4, P, 6 8, Br, 8 7 $C_{36}H_{29}BrO_6P_2Pt$ requires C, 48 35, H, 3 25, P, 6 9 Br, 8 95%) *Bromo[tri-o tolyl phosphito(2C,P)](tri-o-tolyl phosphite)platinum*(II) as white microneedles, 80% m p 199—200° (Found C 51 7, H, 4 05, P, 6 6, Br 7 9 $C_{42}H_{41}BrO_6P_2Pt$ requires C 51 55, H 4 2 P 6 35 Br 8 15%) *Bromo[tri-p-tolyl phosphito(2C P)](tri-p-tolyl phosphite)platinum*(II) as white lustrous microcrystals, 80% m p 178—180° (Found C, 51 9, H, 4 35, P, 6 25, Br 8 1%, *M*, 981 $C_{42}H_{41}BrO_6P_2Pt$ requires C, 51 55 H, 4 2, P, 6 35 Br, 8 15% *M*, 978)

Attempted Reaction of Di-iodobis(triphenyl phosphite)-platinum(II) *in Boiling Decalin* —The complex (0 3 g) was heated under reflux in decalin for 4 h Only trace amounts of hydrogen iodide were eliminated and, on cooling the reaction mixture at 0° overnight, unchanged di-iodobis-(triphenyl phosphite)platinum was recovered (0 24 g, 80%) (Found C, 40 6 H, 2 95 I, 23 55 $C_{36}H_{30}I_2O_6P_2Pt$ requires C, 40 45 H, 2 95 I 23 75%)

Di-iodobis(tri-*o*-tolyl phosphite)platinum(II) was similarly recovered unchanged and in 80% yield after heating under reflux in decalin for 4 h (Found C, 43 55, H, 3·8, I, 21 35 $C_{42}H_{42}I_2O_6P_2Pt$ requires C, 43·75, H, 3 65, I, 21·95%)

Prolonged Reaction of Di-iodobis(triphenyl phosphite)-platinum —The complex (0·3 g) was heated under reflux in decalin for 72 h, hydrogen iodide (0·6 mol) was evolved The reaction mixture was cooled at 0° overnight and the pale yellow solid (0·2 g) deposited was collected by filtration and washed with n-hexane This solid product was identified by spectroscopic methods as a mixture of $PtI_2[P(OPh)_3]_2$ and the metallated derivative $PtI[(PhO)_2P(OC_6H_4)][P(OPh)_3]$

Attempted Dimetallation of Dichlorobis(triphenyl phosphite)platinum —Dichlorobis(triphenyl phosphite)platinum (0 7 g) was heated under reflux in decalin (8 ml) Hydrogen chloride evolution (*ca* 1 mol) occurred during the first 12 h and virtually ceased thereafter After 5 days the reaction solution was cooled at 0° overnight, and the resultant precipitate (0 4 g, 60%) filtered off and washed with n-hexane The product was identified spectroscopically as the mono-metallated derivative

Deplatination Reactions —Chloro[tri-*o*-tolyl phosphito-(2*C*,*P*)](tri-*o*-tolyl phosphite)platinum (0 20 g) dissolved in dichloromethane (35 ml) was saturated with hydrogen chloride gas for 10 min, then sealed and set aside for 24 h The solution was partially evaporated then diluted with n-hexane (20 ml) to induce crystallisation The white crystalline product (0 17 g, 82% based on platinated complex) was washed with n-hexane, dried *in vacuo* and characterised as dichlorobis(tri-*o*-tolyl phosphite)platinum by i r and ^1H n m r spectroscopy

Under similar conditions chloro[triphenyl phosphito-(2*C*,*P*)](triphenyl phosphite)platinum reacted to give dichlorobis(triphenyl phosphite)platinum (77%), characterised by i r spectroscopy

Palladation Reactions

Chloro[triphenyl phosphito(2C,P)](triphenyl phosphite)-palladium(II) —Dichlorobis(triphenyl phosphite)palladium (0 4 g, 0 0005 mol) was heated in decalin under reflux for 3 h The hot solution was filtered to remove precipitated palladium metal then cooled overnight at room temperature The precipitate was washed thoroughly with n-hexane then dried *in vacuo* to give the required product (0 18 g, 50%) Recrystallisation from dichloromethane–methanol gave white microcrystals (m p 143°) (Found C, 57 1, H, 3·75, P, 7 9, Cl, 4 45%, *M*, 694 $C_{36}H_{29}ClO_6P_2Pd$ requires C 56 8, H, 3 85, P, 8 15 Cl, 4 65%, *M*, 761)

The following were similarly prepared *Chloro[tri-o-tolyl phosphito(2C,P)](tri-o-tolyl phosphite)palladium*(II) as white microneedles, 50%, m p 154—155° (Found C, 59 85, H 4 65, P, 7·1, Cl, 4 4 $C_{42}H_{41}ClO_6P_2Pd$ requires C, 59 65 H, 4 9, P, 7 35, Cl, 4 2%) *Chloro[tri-m-tolyl phosphito-(2C,P)](tri-m-tolyl phosphite)palladium*(II) as white microneedles, 50%, m p 193—194° (Found C, 59 75, H, 4 8 P, 7 1, Cl, 4·5 $C_{42}H_{41}ClO_6P_2Pd$ requires C, 59 65, H 4 9, P, 7 35, Cl, 4 2%) *Chloro[tri-p-tolyl phosphito-(2C,P)](tri-p-tolyl phosphite)palladium*(II) as white microcrystals, 50%, m p 138—141° (Found C, 59 75, H, 5 05 P, 7 0, Cl, 4 45 $C_{42}H_{41}ClO_6P_2Pd$ requires C, 59 65 H 4 9, P, 7 35, Cl, 4 2%) *Chloro[tri-p-chlorophenyl phosphito(2C,P)](tri-p-chlorophenyl phosphite)palladium*(II) as white microneedles 80% (Found C 44 8 H, 2 3 Cl 25 2 $C_{36}H_{23}Cl_7O_6P_2Pd$ requires C 44 65 H, 2 4, Cl 25 6%)

Bromo[tri-o-tolyl phosphito(2C,P)](tri-o-tolyl phosphite)-palladium(II) —Dibromobis(tri-*o*-tolyl phosphite)palladium (0·3 g) was heated under reflux for 3 h in decalin (5 ml) The hot solution was filtered to remove precipitated palladium metal, then cooled overnight at room temperature Well formed crystals of required product (pale yellow) and unchanged starting material (orange) were isolated from the mother liquor, washed by decantation, then separated manually Yield 20% (m p 151°) (Found C, 56·45, H, 4·7, P, 7·0, Br, 8·8 $C_{42}H_{41}BrO_6P_2Pd$ requires C, 56·7, H, 4·65, P, 6·95, Br, 9·0%)

Other palladium(II) dibromo complexes $PdBr_2[P(OAr)_3]_2$ reacted under similar conditions to give mixtures of product and starting material These were identified by ^1H n m r spectroscopy but could not be separated by crystallisation

*Attempted Palladation of Di-iodobis(tri-*p*-tolyl phosphite)-palladium*(II) *in Boiling Decalin* —The complex (0·2 g) was heated in decalin under reflux for 4 h, only trace amounts of hydrogen iodide were evolved The hot solution was filtered to remove metallic palladium, then cooled to room temperature overnight Unchanged di-iodobis(tri-*p*-tolyl phosphite)palladium precipitated from the solution and was recovered (0·18 g, 90%) (Found C, 47·6, H, 3·95, I, 23·0 $C_{42}H_{42}I_2O_6P_2Pd$ requires C, 47·35, H, 4·0, I, 23·8%)

Depalladation Reaction —Chloro[tri-*o*-tolyl phosphito-(2C,*P*)](tri-*o*-tolyl phosphite)palladium(II) (0·20 g) dissolved in dichloromethane (35 ml) was saturated with hydrogen chloride gas for 10 min The colourless solution rapidly turned deep yellow, the characteristic colour of $PdCl_2[P(OAr)_3]_2$ complexes in dichloromethane solution The solution was concentrated by evaporation, then diluted with n-hexane (15 ml) to induce crystallisation The yellow crystalline product (0·185 g, 88% yield based on palladated complex) was washed with n-hexane, dried *in vacuo* and characterised as dichlorobis(tri-*o*-tolyl phosphite)palladium by i r and ^1H n m r spectroscopy

Under similar conditions chloro[triphenyl phosphito-(2C,*P*)](triphenyl phosphite)palladium(II) (0 20 g) reacted to give dichlorobis(triphenyl phosphite)palladium (0·15 g, 72%), characterised by i r spectroscopy

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SHORT COMMUNICATION

Physico-chemical studies on the interaction of L-lysine with some transition metals having abnormal oxidation states

OMAR FAROOQ, ANEES UDDIN MALIK and NASEER AHMAD
Inorganic Research Laboratory, Chemistry Department, Aligarh Muslim University, Aligarh U.P. (India)
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The recent literature on α-amino acid complexes abounds with references pertaining to various aspects of this field, especially the determination of the stability and elucidation of the structure of amino acid complexes with transition metals[1–5] particularly, Ni^{2+}, Cu^{2+}, Cr^{3+} and Co^{2+} ions. The earlier investigations on the metal amino acid complexes based upon potentiometric and pH-metric titrations were carried out by Albert[6] and Perkin[7]. Albert modified Bjerrum's method[8] for the determination of stability constants. The complexes of transition metals with amino acids are of interest because of their biological importance and the presence of potential coordinating amino and carboxylic groups. However, very few papers deal with the interaction of α-amino acids with transition metals having unusual oxidation states. Recently, a detailed study of this aspect of the problem was undertaken by the authors and the complexes of Cr^{2+}, UO_2^{2+}, VO^{2+} and Ti^{3+} with various amino acids were studied[9–11].

The present communication deals with the interaction of Cr^{2+}, UO_2^{2+}, VO^{2+} and Ti^{3+} with an essential amino acid, L-lysine. The metal–amino acid molar ratio was ascertained by conductometric or potentiometric titrations and the stability constants of these complexes were computed from the results of pH-metric titrations in aqueous medium. The values of ΔF° were calculated from the relation $\Delta F^\circ = -RT \ln K_s$. The complexes with VO^{2+} and UO_2^{2+} were isolated and analysed, but the complexes with Ti^{3+} and Cr^{2+} could not be isolated in pure state due to the high susceptibility of these ions towards atmospheric oxidation.

Experimental

The amino acid, L-lysine (biologically pure, Fluka, Switzerland) was used for these experiments, and the solutions were prepared in doubly distilled air-free water.

Chromium(II) chloride was prepared by the method of Bathis and Bailer[12]. The aqueous solution was prepared as described previously, and stored in an airtight storage vessel under an atmosphere of oxygen-free nitrogen. The solution was standardised potentiometrically by titration with standard copper sulphate. The strength was checked periodically before use.

Uranyl sulphate and vanadyl sulphate (AnalaR, B.D.H., England) were

employed and their solutions were standardised by gravimetric estimation of the metals as oxides[13,14].

An aqueous solution of titanium(III) chloride was prepared by dissolving crystals[15] of $TiCl_3 \cdot 6H_2O$ in air-free doubly distilled water. The solution was also standardised[16]. Fresh solutions were always prepared before use and kept covered with a layer of Kerosene oil or toluene throughout the investigations to avoid oxidation. Carbonate free KOH was used to prepare its aqueous solution and the latter was kept in a Pyrex bottle fitted with a guard tube containing KOH for protection against atmospheric carbon dioxide. The solution was standardised by titrating with standard oxalic acid and checked periodically before carrying out the pH-metric titrations.

The potentiometric titrations were carried out with a Tinsley potentiometer having a lamp and scale arrangement and using platinum and calomel as indicator and reference electrodes, respectively. The pH-metric titrations were performed with a direct reading EIL pH meter, model 23A (England). All the titrations were carried out in a specially designed cell, with provision for adding metal salt solutions and KOH from the burettes, to a stirred oxygen-free system. The conductometric titrations were performed using a Philips conductivity Bridge (India), model PR9500/90 and a dip type cell (cell factor 1.48).

Results and discussion

The molar ratio of the interaction of vanadyl, uranyl and titanous ions with L-lysine determined conductometrically was 1:2 (amino acid:metal). Potentiometric titrations exhibit the same ratio for chromium(II) chloride–lysine systems.

The pH-metric titrations were performed in order to evaluate the stability constants of the various complexes formed by the union of L-lysine and metal ions. These titrations were performed in triplicate for each system in the order: (a) amino acid, 10^{-2} mol dm^{-3}, (b) metal salt, 5×10^{-3} mol dm^{-3} and (c) metal salt and amino acid, equimolar (total concentration 5×10^{-3} mol dm^{-3} and 10^{-2} mol dm^{-3}, respectively) using 0.1 *M* KOH as titrant. In case of trivalent titanium chloride, the concentration of the metal was kept at 3.3×10^{-3} mol dm^{-3} in the mixture. The pH-metric titration curves show appreciable shifts indicating thereby the formation of a complex with the amino acid. The complex formation, or equilibrium constants, K', K'' and the overall stability constant, K_s were evaluated by the following method.

The stepwise complex formation between a divalent metal ion, M^{2+} and amino acid resulting in the formation of species MA^+ and MA_2 can be explained by the following equations:

$$NH_3^+ ACOO^- + M^{2+}Cl_2^- \overset{K'}{\rightleftharpoons} [MNH_2ACOO^-]^+ Cl^-$$

$$NH_3^+ ACOO^- + [MNH_2ACOO^-]^+ Cl^- \overset{K''}{\rightleftharpoons} [M(NH_2ACOO^-)_2]^0 + H^+ + Cl^-$$

Assuming the ionization of the amino group as

$$NH_3^+ ACOO^- \overset{k_a}{\rightarrow} NH_2ACOO^- + H^+ ,$$

the values of the first and second formation or equilibrium constants K' and K'' may be given as,

$$K' = [MA^+]/[M][A^-] \quad (1)$$

$$K'' = [MA_2]/[MA^+][A^-] \quad (2)$$

and the overall stability constant, $K_s = K'K'' = [MA_2]/[M][A^-]^2$. As complex formation proceeds, H^+ ions are liberated, and the measurements of the concentration of these ions provide a means of estimating the extent of complex formation.

As the concentration of free metallic ion is not measured by this method, the values of K' and K'' can be written as

$$K' = \bar{n}/(1-\bar{n})[S_c] \quad (3)$$

$$K'' = (\bar{n}-1)/(2-\bar{n})[S_c] \quad (4)$$

where $[S_c]$ is the concentration of coordinating species and $\bar{n}$ is the average number of molecules of complex forming agent bound by one atom of the metal. Values of $[S_c]$ could be obtained from the following relation which holds good for simple amino acids between pH 3 and 11.

$$\log [S_c] = (pH - pK_a) + \log \{[HS_c^0] - [KOH]\} \quad (5)$$

where $[HS_c^0]$ is the concentration of the complex forming agent before metal is added. [KOH] is the concentration of potassium hydroxide which would be present if the complex forming agent and metal were absent, and pK_a is the ionization constant of the equilibrium

$$NH_3^+ACOO^- \rightleftharpoons NH_2ACOO^- + H^+$$

The values of $\bar{n}$ can be evaluated by the greatly simplified equation

$$\bar{n} = 2[KOH]/[HS_c^0] \quad (6)$$

From the plots of $\log [S_c]$ *vs.* $\bar{n}$ (formation curves) given in Fig. 1 for various lysine–metal systems, the values of $-\log [S_c]$ have been evaluated at $\bar{n} = 1$, subsequently, the values of $\log K_s$ were obtained by applying the relation, $\log K_s = -2 \log [S_c]$. The values of $\log K_s$ determined graphically as well as by calculation are given in Table 1.

The values of the overall stability constants obtained from the formation curves (Fig. 1) are in good agreement with those calculated by applying the above relations. The uranyl sulphate–lysine complex has the highest $\log K_s$ value, the chromium(II) chloride and vanadyl sulphate complexes have almost the same stabilities, and the titanium(III) chloride complex has the lowest $\log K_s$ value. The values of $-\Delta F^\circ$ were found to be 57.8, 56.4, 57.7 and 58.0 kJ mol^{-1} for the Cr^{2+}, Ti^{3+}, VO^{2+} and UO_2^{2+} systems respectively.

These observations could not be quantitatively substantiated in the case of the chromium(II) chloride and titanium(III) chloride complexes as no information could be obtained as to the nature of the bonding since the complexes could not be isolated in a pure state owing to the highly susceptible nature of these metal ions towards oxidation. However, in the case of vanadyl sulphate and uranyl sulphate the solid compounds had a ratio of 1:2 (lysine:metal) on the basis of elemental analyses. The general formula may be given as $M_2L \cdot nH_2O$, where M = $VOSO_4$ or UO_2SO_4 and $n = 2$ and 7 respectively. L is L-lysine, $NH_2(CH_2)CH(NH_2)$-COOH. This supports the conclusion drawn by the conductometric titrations which

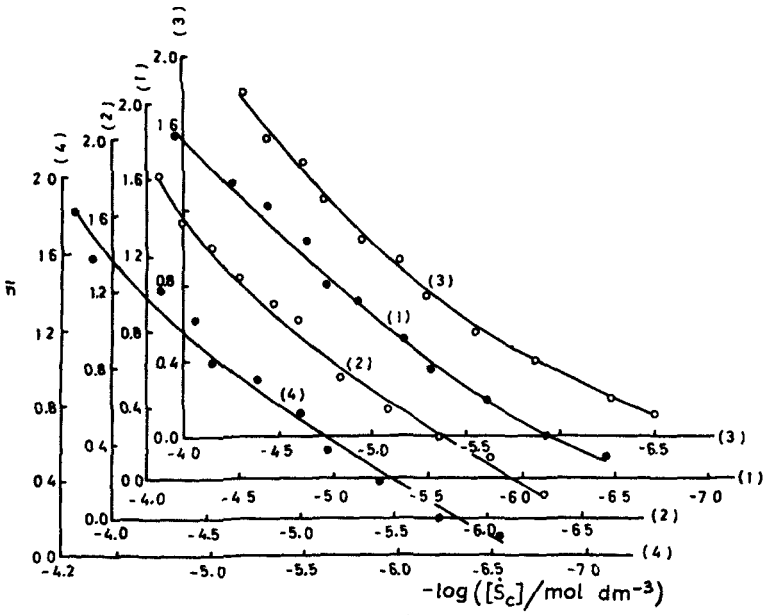

Fig. 1. Formation curves for the systems: (1), L-lysine–chromium(II) chloride; (2), L-lysine–titanium-(III) chloride; (3), L-lysine–vanadyl sulphate; (4), L-lysine–uranyl sulphate.

TABLE 1

VALUES OF LOG K_s FOR COMPLEXES OF L-LYSINE WITH Cr^{2+}, Ti^{3+}, VO^{2+} AND UO_2^{2+}

Complex	*Log (K_s/dm^3 mol^{-2})*	
	By calculation	*By graphical procedure*
Chromium(II) chloride–L-lysine	10.11	10.12
Titanium(III) chloride–L-lysine	9.88	9 92
Vanadyl sulphate–L-lysine	10.09	10.04
Uranyl sulphate–L-lysine	10.19	10.09

indicate a molar ratio of 1:2 (lysine:metal) in these complexes. Other related studies on various amino acid systems are in progress.

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SHORT COMMUNICATION

Stability of some amino acid complexes with palladium(II) using sodium chloropalladite

OMAR FAROOQ, NASEER AHMAD and ANEES UDDIN MALIK*

Inorganic Research Laboratory, Chemistry Department, Aligarh Muslim University, Aligarh/U.P. (India)

(Received 22nd May 1973)

The ability of amino acids to form metal complexes is not only of theoretical importance but of very great practical significance. A number of papers dealing with the interaction of amino acids with transition metals are reported in the existing literature. The studies are based upon various physico-chemical techniques[1–7]. Recently a systematic examination of the coordinating ability of amino and carboxylic groups was undertaken by the authors, and complexes with Cr^{2+}, UO_2^{2+}, VO^{2+}, Ti^{3+}, $[Pd(Tu)_4]Cl_2$** and rare-earths were studied[8–13]. From the literature it appears that no efforts have yet been made to study the stability of the amino acids with palladium(II) using sodium chloropalladite and employing Bjerrum's method[14].

The present communication deals with the interaction of sodium chloropalladite with various amino acids including two sulphur-containing materials, based upon potentiometric and pH-metric measurements. The values of ΔF^0 were computed from the relation $\Delta F^0 = -RT \log K_s$ at 27°C.

Experimental

The amino acids glycine, DL-α-alanine, DL-serine, DL-valine, L-leucine, L-proline, L-asparagine, DL-methionine and taurine (BDH biologically pure products) were used in these investigations and their solutions were prepared in doubly distilled air-free water.

Sodium chloropalladite (Johnson Matthey, London) was used to prepare solutions which were standardised gravimetrically using dimethylglyoxime as the precipitating agent[15]. Carbonate-free KOH solution was used for pH-metric titrations. The stock solution was stored in a Pyrex flask fitted with a KOH tube to remove atmospheric CO_2. The strength of the solution was checked before carrying out a particular set of titrations.

The pH-metric titrations were performed using a direct reading Elico pH-meter, model LI-10 (India) in conjunction with glass and calomel electrodes. All these titrations were performed in a specially designed cell[16] at 27°C in an oxygen-free atmosphere. The potentiometric titrations were performed with a Toshniwal

* Present address: Department of Material Science and Metallurgy, University of Liverpool, Liverpool, England

** Tu stands for the thiourea molecule.

Titration Potentiometer, type CL06 (India), using platinum and calomel as indicator and reference electrodes.

Results and discussion

When an aqueous solution of potassium chloropalladite reacts at room temperature with two moles of amino acid (glycine), yellow prisms of $[Pd(Gly)_2]\cdot 3H_2O$ separate quickly, together with glistening light yellow plates with the same composition except that water of crystallisation[17] is absent. Potentiometric studies in aqueous medium also revealed a molar ratio of 1:2 (metal:amino acid) in the case of glycine, DL-α-alanine, DL-serine, DL-valine, L-leucine, L-proline and L-asparagine. In the case of sulphur-containing amino acids, DL-methionine and taurine (sulphonic group), a similar behaviour was observed.

The complexes of a metal with various chelating agents may exist in varying states of stability, as may the complexes of various metals with the same chelating agent. The association of the various amino acids with metals followed a stepwise mechanism and pH-metric titrations were employed to determine stability or its converse, dissociation. The experimental procedure has generally been to titrate a solution containing two equivalents of the amino acid (A) and one mole of the bivalent metal salt, Pd^{2+} (thus a ratio of amino acid to metal 2:1) with standard KOH (carbonate-free) under anaerobic conditions, and to measure the pH after each addition of alkali.

The equilibria in the reaction involving stepwise complex formation by the union of M^{2+} (metal) and amino acid (A) whereby MA^+ and MA_2 are formed may be expressed as

$$NH_3^+ACOO^- + M^{2+}Cl_2^- \overset{K_1}{\rightleftharpoons} [MNH_2ACOO^-]^+Cl^- + H^+ + Cl^-$$

$$NH_3^+ACOO^- + [MNH_2ACOO^-]^+Cl^- \overset{K_2}{\rightleftharpoons} [M(NH_2ACOO^-)_2]^0 + H^+ + Cl^-$$

In these systems the ionisation of the amino group is involved, namely

$$NH_3^+ACOO^- \overset{K_2}{\rightleftharpoons} NH_2ACOO^- + H^+$$

$$K_1 = [MA^+]/[M][A^-] \qquad K_2 = [MA_2]/[MA^+][A^-]$$

For the overall stability constant,

$$K_s = K_1K_2 = [MA_2]/[M][A^-]^2$$

The overall dissociation constant will of course be $K_d = 1/K_s$. Hydrogen ions are liberated, as complex formation proceeds, and the concentration of these ions provides a measure of the degree of complex formation.

A simple and modified method was developed by Albert[18] to evaluate the overall stability constant. Thus

$$\bar{n} = [MA^+] + 2[MA_2]/[M] + [MA^+] + [MA_2]$$

where $\bar{n}$ is defined as the average number of molecules of amino acid bound by one atom of metal. The value of $\bar{n}$ starts at nearly zero, and reaches a maximum in all the present cases of approximately 2. At this juncture a very unstable complex species MA_3^+ makes its appearance. The error in this region (MA_3^+ species, $\bar{n}$ above

2) of the curve is too high and most workers agree as to the order of magnitude of this possible species[19]. When $\bar{n}=1$,

$$[MA^+]+2[MA_2]=[M]+[MA^+]+[MA_2]$$

whereupon $[M]=[MA_2]$ and the values of K_1 and K_2 may be rewritten as

$$K_1=\bar{n}/(1-\bar{n})[Sc] \qquad K_2=(\bar{n}-1)/(2-\bar{n})[Sc]$$

where [Sc] is the concentration of complexing species and the value of [Sc] may be computed from the following relation which is valid between pH 3 and 11 for simple amino acids:

$$\log[Sc]=(pH-pK_a)+\log([HSc^0]-[KOH])$$

where $[HSc^0]$ is the concentration of the amino acid before the metal is added. [KOH] is the concentration of alkali which would be present in the solution after each gradual addition, if both the metal and the amino acid were absent.

The correct value for log[Sc], corresponding to the point where $\bar{n}=1$, was evaluated graphically after plotting $\bar{n}$ *vs.* $-\log[Sc]$. These values of $\bar{n}$ may be calculated from the modified general relation,

$$\bar{n}=2[KOH]/[HSc^0]$$

The plots of $\bar{n}$ *vs.* $-\log[Sc]$ (formation curve) are given in Fig. 1 for a few amino acid–Na_2PdCl_4 systems. The values of $\log K_s$ determined by these two methods and ΔF^0 at 27°C are listed in Table 1.

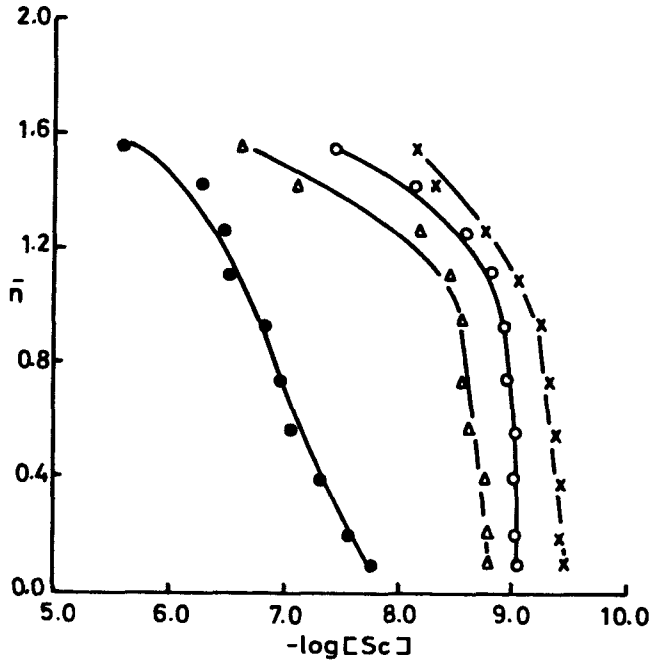

Fig. 1. Formation curves. (●) Taurine–Na_2PdCl_4 system; (△) DL-methionine–Na_2PdCl_4 system; (○) glycine–Na_2PdCl_4 system; (×) DL-α-alanine–Na_2PdCl_4 system.

TABLE 1

VALUES OF log K_s AND ΔF^0 FOR NINE AMINO ACID—Na_2PdCl_4 SYSTEMS

Systems	*log (K_s/mol^2 l^{-2})*		ΔF^0/*kcalmol*$^{-1}$ [a]
	Graphically	*Calcd*	
Glycine–Na_2PdCl_4	17 50	17 58	240 3
DL-α-alanine–Na_2PdCl_4	18 12	18 17	255 8
DL-serine–Na_2PdCl_4	16 84	16 88	230 1
DL-valine–Na_2PdCl_4	17 52	17 54	240 0
L-leucine–Na_2PdCl_4	18 20	18 22	249 2
L-proline–Na_2PdCl_4	15 70	15 66	214 2
L-asparagine–Na_2PdCl_4	15 12	15 11	206 0
DL-methionine–Na_2PdCl_4	17 00	16 97	226 8
Taurine–Na_2PdCl_4	13 40	13 34	178 0

[a] 1 cal = 4 184 J

The values of log K_s computed from formation curves are in good agreement with those calculated. The values of log K_s vary from taurine (13.40, 13.34) to L-leucine (18.20, 18.22), whereas the values of glycine (17.50, 17.58) and DL-valine (17.52, 17.54) are almost the same. There does not seem to be any definite correlation between the nature of amino acids and the K_s values. However, in the case of sulphur-containing amino acids, the value of log K_s decreases as the distance between amino and carboxylic groups increases (between NH_2 and SO_2OH in the case of taurine). The value of log K_s for taurine is the lowest in these studies. These values are higher than those in the systems studied earlier[8–10,12,18]. It is probably due to the high affinity of palladium(II) towards amino acids. A similar behaviour was observed in the case of Cu^{2+}–amino acid systems. To obtain the lower values of $\bar{n}$ for Pd^{2+} it was necessary to perform an additional titration with acid, as suggested by Albert[18] for the case of Cu^{2+} complexes with amino acids The real nature of bonding in these complexes is a matter of speculation as no complex could be isolated in a sufficiently pure state. Further studies on related systems are in progress.

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SHORT COMMUNICATION

Studies on the mode of interaction of iridium(IV) with amino acids using sodium chloroiridate

OMAR FAROOQ and NASEER AHMAD

Inorganic Research Laboratory, Department of Chemistry, Aligarh Muslim University, Aligarh/U.P. (India)

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The equilibria between metal ions and amino acids in solutions of various concentrations have been studied by a number of workers[1–4]. Due to the biological significance and the coordinating ability of amino and carboxylic groups, the interaction of the transition metal ions with amino acids covers a wide area of investigation[5–9]. The behaviour of transition metals having unusual oxidation states towards certain amino acids was reported by the authors in earlier communications[10–16]. The present study deals with the determination of the stability constants and composition of certain amino acid–iridium(IV) systems formed using sodium chloroiridate. These studies are based upon pH-metric titration under anaerobic conditions. The values of ΔF^0 are computed from the relation $\Delta F^0 = -RT \log K_s$. All studies were carried out at 35°C.

Experimental

Amino acids such as glycine, DL-α-alanine, L-asparagine, DL-serine, DL-valine, L-proline, taurine (BDH, biologically pure), β-alanine, DL-phenylalanine, DL-methionine and DL-threonine (E. Merck) were used and their solutions were prepared in doubly distilled air-free water. Sodium chloroiridate (Johnson Matthey, England) in solution was standardised by the method developed by Barefoot *et al.*[17].

The pH-metric titrations were performed with a direct reading Elico pH-meter, model LI-10 (India) and potentiometric titrations with the help of a Toshniwal Titration Potentiometer, model CL06 (India). Glass and saturated calomel electrodes were utilised as reference and indicator electrodes respectively. All studies were carried out in a specially designed cell as described previously[19].

Results and discussion

Potentiometric titrations revealed a ratio of 1:4 (metal:amino acid) in all the cases. The pH-metric titrations were performed as described in earlier communications[7,10,18]. One equivalent of carbonate-free KOH of 0.1 *M* was used as a titrant. Iridium being tetravalent in nature, its concentration was kept at 0.0025 *M* in all the systems, whereas the concentration of amino acid was constantly kept at 0.01 *M*. The values of partial stability constants (log K' and log K'') and overall stability constants (log K_s) are listed in Table 1.

TABLE 1

PARTIAL AND OVERALL STABILITY CONSTANTS

Systems	*Average log K'*	*Average log K''*	*log (K_s/mol^2 l^{-2})*		*ΔF^0/kcal mol^{-1}*[a]
			Graphically	*Calcd.*	
Glycine–Na_2IrCl_6	3.15	2.63	5.70	5.78	81.27
DL-α-Alanine–Na_2IrCl_6	4.36	2.61	7.02	6.97	99.59
L-Asparagine–Na_2IrCl_6	3.22	2.68	5.85	5.90	82.92
DL-Serine–Na_2IrCl_6	6.83	3.32	9.75	9.85	138.40
DL-Valine–Na_2IrCl_6	3.71	2.76	6.42	6.47	95.85
β-Alanine–Na_2IrCl_6	6.76	3.19	9.90	9.95	139.70
DL-Phenylalanine–Na_2IrCl_6	5.28	2.53	7.76	7.81	109.70
DL-Threonine–Na_2IrCl_6	5.47	3.49	8.92	8.96	125.60
DL-Taurine–Na_2IrCl_6	4.72	3.05	7.80	7.77	109.10
DL-Methionine–Na_2IrCl_6	7.30	3.11	10.36	10.41	146.20

[a] 1 cal = 4.184 J.

The amino acids were found to produce highly soluble complexes with metals. However, in the case of L-proline and L-leucine it was difficult to get the correct values of the partial stability constants (log K' and log K''). The values obtained deviated a lot from the simple amino acid complexes discussed by various authors. Probably, this was due to the lower solubility of these complexes, on the whole, than those of the other systems involving metal–amino acids. The behaviour of L-proline was also strange and this material needs a thorough investigation.

The majority of the amino acids followed the same sequence as that observed for other amino acid complexes previously[7,9–12,14,15]. In general, at the first stage one atom of the metal combined with one molecule of the amino acid (having two ionising groups, NH_2 and COO^-) and thus the 1:1 complex species, MA^+, did not appreciably react with a second molecule to give the 1:2 complex MA_2^+. This position was attained when the value of $\bar{n}$ (average number of molecules of the amino acid combined with one atom of metal) reached 0.80 or 80% of the 1:1 complex present.

The values of various terms were evaluated from the relations given below:

$$\log K' = \log \bar{n} - \log (1-\bar{n}) - \log [Sc] \quad (1)$$

$$\log K'' = \log (\bar{n}-1) - \log (2-\bar{n}) - \log [Sc] \quad (2)$$

$$\log K_s = \log \bar{n} - \log (2-\bar{n}) - 2 \log [Sc] \quad (3)$$

$$\log K_s = 2 \log [Sc], \text{ when } \bar{n} = 1.00 \quad (4)$$

and

$$\log K_s = \log K' + \log K'' \quad (5)$$

$$\log [Sc] = (pH - pK_a) + \log ([HSc^0] - [KOH]) \quad (6)$$

where $\bar{n} = 2[KOH]/[HSc^0]$; $[HSc^0]$ = concentration of the complex-forming species.

Equations (1) and (2) give regular values of log K' and log K''. The ranges

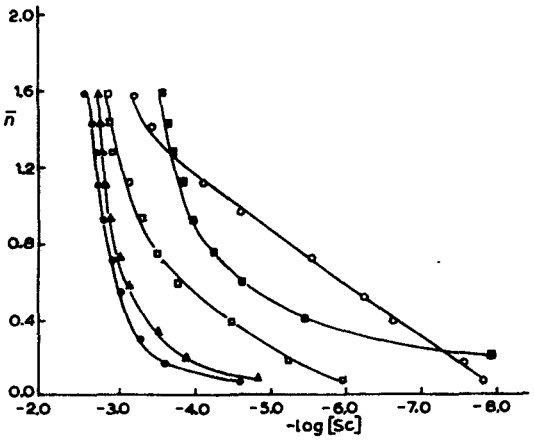

Fig. 1. Formation curves. (●) Glycine–Na_2IrCl_6 system; (▲) L-asparagine–Na_2IrCl_6 system; (□) DL-α-alanine–Na_2IrCl_6 system; (■) DL-serine–Na_2IrCl_6 system; (○) taurine–Na_2IrCl_6 system.

are: log K' ($\bar{n}=1.00$–0.80) and log K'' ($\bar{n}=1.26$–1.80) respectively, in all the cases reported herein. The values of the overall stability constant, log K_s, obtained from the formation curves (Fig. 1) are in good agreement with those calculated employing the above relations. In the present study, the stability of these systems varies from 5.78 for glycine to 9.95 for β-alanine. It is interesting to compare the stabilities of the complexes of DL-α-alanine, β-alanine and DL-phenylalanine. The order is: β-alanine(9.95) > DL-phenylalanine(7.81) > DL-α-alanine(6.97). It is obvious that the NH_2 group at the β-position is more basic in nature than the NH_2 group at the α-position.

In the case of L-proline and L-leucine, the values of the stability constant could not be calculated correctly. The plot of $\bar{n}$ *vs.* $-\log$ [Sc] also indicated the absence of appreciable quantity of the 1:1 complex species, MA^+, even in the first portion of the titration curve. Equations (3) and (4) hold good regardless of the nature of the system. Equation (3) holds good between pH 3 and 11.0 whereas eqn. (4) is valid only when $\bar{n}=1.00$.

In the case of sulphur-containing amino acids, the value of log K_s for DL-methionine is higher than that for taurine. In general, the value of log K_s decreases as the distance between the amino and carboxylic groups increases (between NH_2 and SO_2OH in the case of taurine). The present study does not clarify the part played by the sulphur atom. The actual mode of coordination in these complexes is a matter of speculation. The observations could not be quantitatively substantiated due to the lack of information since it was not possible to isolate a complex in a sufficiently pure state.

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Cinchonine Complexes of Titanium(III) & Copper(II)

MOHD MAHFOOZ KHAN, S. M. F. RAHMAN & NASEER AHMAD
Department of Chemistry, Aligarh Muslim University
Aligarh

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Complexes of cinchonine with copper(II) and titanium(III) chlorides, having a molar ratio of 1:1 (metal: ligand) and two associated water molecules have been prepared. Potentiometric and conductometric studies give a molar ratio of 1:1 and 2:1 (metal· ligand) in ethanol. The magnetic moments of the complexes are found to be 1·84 and 1·1 B.M. respectively. IR studies indicate that the ligand coordinates through the nitrogen of the heterocyclic ring in both the complexes. Thermogravimetric analysis and IR spectra show the presence of a coordinated and a lattice held water molecule in Cu(II) complex and two lattice held water molecules in Ti(III) complex.

VERY little work has been done on the complexes of cinchonine, perhaps due to the complicated structure of the ligand. Seshadri and Rao[1] have prepared organo-mercury compounds with quinine and cinchonine. Circulis and Straumanis[2] have reported the formation of cinchonine and cinchonidine tetrazido copper compounds but no structural aspects of the coordination compounds were discussed in these studies. The present communication deals with the conductometric, potentiometric, magnetic moment, spectral and thermogravimetric studies on the hitherto unknown complexes of Cu(II) and Ti(III) chlorides with cinchonine.

A stock solution of Ti(III) chloride was prepared by dissolving crystallized $TiCl_3.6H_2O$ (ref. 3) in ethanol and standardized by the indirect permanganate titration[4]. $CuCl_2.2H_2O$ crystals (BDH, AR) were dissolved in ethanol and the solution standardized against standard thiosulphate solution. A standard cinchonine solution in ethanol was prepared by accurate weighing.

Reverse conductometric titrations were performed using Philips conductivity bridge, model PR 9500, in ethanolic solution. Potentiometric titrations were carried out using a Toshniwal potentiometer type CL06, provided with a platinum electrode in conjunction with a calomel electrode. Readings were taken with a time interval of 2 min after each successive addition of cinchonine solution to the metal salt solution.

The magnetic susceptibility of the solid Cu and Ti complexes was measured at room temperature by Gouy method. The IR spectra of cinchonine and its complexes were recorded on a Perkin-Elmer infracord, model 221, in KBr discs in the range of 4000-250 cm^{-1}. The TGA curves were obtained between room temperature and 600° at a heating rate of 3°/min.

Preparation of the complexes — Cu(II) chloride solution in tetrahydrofuran was added to 100 ml of cinchonine solution in the same solvent till a copious amount of the precipitate was formed. Addition of excess metal solution was avoided since it results in the dissolution of the precipitate. The precipitate was centrifuged, washed several times with tetrahydrofuran to remove excess metal salt or cinchonine and dried *in vacuo* (Found: C, 48·08; H, 5·40; N, 5·88; Cl, 15·42; Cu, 13·28. $C_{19}H_{22}ON_2.CuCl_2.2H_2O$ requires C, 49·04; H, 5·59; N, 6·02; Cl, 15·27; Cu, 13·65%). Ti(III) complex was prepared by a similar procedure (Found: C, 46·94; H, 5·09; N, 5·79; Cl, 21·90; Ti, 9·71. $C_{19}H_{22}ON_2.TiCl_3.2H_2O$ requires C, 47·02; H, 5·36; N, 5·77; Cl, 21·96; Ti, 9·89%).

The complexes of Ti(III) and Cu(II) are light yellow and dirty green respectively. The complexes are water soluble and slowly hydrolyse in water.

The complexes have 1:1 stoichiometry. The results are further confirmed by the potentiometric titrations. However, the conductometric titrations performed using cinchonine in the cell, indicate the formation of 1:1 and 2:1 (metal: ligand) complexes species The formation af 1:1 and 2:1 complex may be explained if it is assumed that the two nitrogen atoms, one heterocyclic and the other belonging to the quinuclidine ring of cinchonine are involved in coordination.

The magnetic monents for Cu(II) and Ti(III) complexes are 1·84 and 1·10 B.M. respectively indicating the presence of one unpaired electron. However, the low value of Ti(III) complex is difficult to explain[5,6].

The three sharp bands at 3070(vs), 3040(s) and 3000(s) cm^{-1} in the IR spectrum of cinchonine are assigned to OH stretch of secondary OH group. On complexation with Cu(II) and Ti(III), the position of these bands is shifted to 3420-3400 and 3190 cm^{-1} respectively. The spectrum of copper complex shows a band at 3060 cm^{-1} which is absent in the spectra of cinchonine and Ti(III) complex. This characteristic band may be due to the ν_{OH} of coordinated water[7]. Cu and Ti complexes show bands of variable intensities in the region 925(s) and 915(vw) cm^{-1} respectively. The strong band at 925 may be due to the bending mode of coordinated water whereas the band at 915 cm^{-1} in Ti complex is too weak to be assigned to coordinated water. The conclusion drawn regarding the presence of coordinated water in Cu(II) complex is in conformity with OH bands reported for a number of complexes[8], e.g. $[Ni(gly)_2]2H_2O$ at 795 cm^{-1}, $Cu(SO_4{\cdot}5H_2O$ at 875 cm^{-1} and $K[Cr(OX)_2(H_2O)_2].3H_2O$ at 1012 and 965 cm^{-1}. The H-O-H bending modes of lattice water occur at 1635(s), 1630(s) and 1620(s) cm^{-1} in the spectra of cinchonine, Ti(III) and Cu(II) complexes respectively.

Besides the above characteristic frequencies, there are two strong bands at 1565 and 1505 cm^{-1} in the spectrum of cinchonine which have been assigned to ν_{CC} and ν_{CN} vibrations of the quinoline ring. On coordination these bands are shifted to 1540 and 1490 cm^{-1} in the case of Ti complex and 1510 and 1455 cm^{-1} in the case of Cu complex.

The peaks due to in-plane deformation vibrations at 1205(s), 1060(w), 1045(s), 1025(s) and 1015(m) cm^{-1} in the spectrum of cinchonine are reduced in number and shifted to lower frequencies with weaker intensities on coordination, viz. 1140(vw) and 1005 (w) cm^{-1} in Ti complex and 1050(m) and 1025(m) cm^{-1} in Cu complex. Similarly, the bands arising due to out-of-plane hydrogen deformation are also reduced in number on coordination. Thus the bands

at 800(s), 780(m), 765(s) and 755(vs) in the spectrum of cinchonine are replaced by the bands at 795 (s) and 760(s) cm^{-1} in the case of both Ti and Cu complexes.

The changes in the ν_{CC}, ν_{CN} and the in-plane and out-of-plane hydrogen deformation and the absence of any change in the region for aliphatic group vibrations (1230-1030 cm^{-1}), clearly indicate that the ligand coordinates through the heterocyclic nitrogen.

TGA analyses of these complexes also corroborate the conclusions drawn about the nature of water molecules present in the complexes. In the case of Cu complex one water molecule is lost around 70°C (theoretical weight loss = 3·85%, observed weight oss = 3·9%) and the second water molecule is lost around 128°C (theoretical weight loss = 7·7%, obseved weight loss = 7·9%). On the other hand, in the case of Ti complex both the water molecules are lost around 105°C (theoretical weight loss = 7·4%, observed weight loss = 7·8%).

On the basis of these observations the complexes may be formulated as $[C_{19}H_{22}O.N_2.CuCl_2.H_2O].H_2O$ and $[C_{19}H_{22}ON_2.TiCl_3].2H_2O$.

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NMR Study of *bis* (thiourea) Cobalt (II) Complexes

H. SINGH, D. K. TYAGI & R. J. SINGH
Department of Physics, Aligarh Muslim University, Aligarh
&
NASEER AHMAD
Department of Chemistry, Aligarh Muslim University, Aligarh

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The chemical shifts of the protons of water and acetone having $Co(tu)_4(NO_3)_2$ and $Co(tu)_4Cl_2$ as solutes at different concentrations were measured. To apply bulk susceptibility correction, susceptibilities of these solutions were also measured. For comparison, the chemical shift of $CoCl_2.6H_2O$ solution in water was also determined. For confident interpretation of the results, conductivities of the complexes in the two solutions were found out at certain concentrations. Structure and behaviour of these compounds in the two solvents at different concentrations were suggested and discussed.

1. Introduction

IN RECENT YEARS, there has been a growing interest in the contact and pseudo-contact shifts. Large chemical shifts of the solvent in solutions containing paramagnetic salts have been attributed to the Fermi-contact term[1]. It was thought worthwhile to investigate the chemical shift of some solutions containing paramagnetic ions as a function of concentration of the solute. To ensure the interpretation of the data on a firm basis, molar conductance and volume susceptibility were also measured. The substances chosen for the study are $Co(tu)_4Cl_2$ and $Co(tu)_4(NO_3)_2$ [where 'tu' stands for thiourea] as they have been recently synthesized[2] and there is some doubt regarding the structure of the latter[2].

2. Experimental Details

For the preparation of the compounds we followed the methods given by Cotton *et al.*[2]

$Co(tu)_4(NO_3)_2$

$Co(NO_3)_2.6H_2O$ (2·91 g, 0·01 mole) was dissolved in 25 ml of butanol, 3·04 g (0·04 mole) of thiourea added and the mixture heated to boiling until all the solid dissolved. The solution changed from red to blue. On cooling, a blue solid separated. This was filtered, washed with ether and recrystallized from ethyl acetate and the crystals dried in vacuum.

$Co(tu)_4Cl_2$

$CoCl_2.6H_2O$ (4·75 g, 0·02 mole) was dissolved in 30 ml of hot butanol and 3·04 g (0·04 mole) thiourea added. The mixture was heated until all the solid dissolved. The solution was allowed to cool to room temperature and benzene was added until a slight permanent turbidity was observed. On further cooling in an ice chest, a blue solid separated and it was filtered, washed and dried in vacuum. The proton magnetic resonance measurements were made on varian high resolution spectrometer (V-4500) operating at 40·00 Mc/s, with a 12-inch electromag e.. The chemical shifts using external reference were measured by side-band technique. The external reference in each case was the solvent. The sample and the reference were maintained at the same height in the cell. The ratio of the length of the sample to the diameter of the cylindrical cell was more than 10 : 1 to meet the condition of infinite length[3].

Conductivity was measured at different concentrations with the help of a Kohlrausch's bridge and the conductance data are given in Table 1.

Magnetic susceptibility was measured by Quincke's method at the concentrations given above. Magnetic moment values were calculated in each case and these values were used to calculate susceptibilities at other concentrations. These susceptibilities at various concentrations were used to correct the observed chemical shifts. The density of these substances was found to be nearly 1·8 g/cc. The inaccuracy in the measurements is about 5%.

3. Results and Discussion

The observed chemical shifts of the solvent proton (acetone and water) as a function of the concentra-

Table 1 — Conductivity Data

Compound	Solute	Solvent	Molar conductance Ω^{-1} cm^2
$Co(tu)_4(NO_3)_2$	2	5·00 ml water	91
	2	5·00 ml acetone	7·7
$Co(tu)_4Cl_2$	1·808	5·00 ml water	100
	0·902	2·00 ml acetone	3·2

tion of solute $Co(tu)_4Cl_2$, $Co(tu)_4(NO_3)_2$ and $CoCl_2 \cdot 6H_2O$ are shown in Fig. 1. In Fig. 2, chemical shift values are plotted against the concentration (after applying bulk susceptibility correction except in the case of $CoCl_2 \cdot 6H_2O$). The molar conductivity values and magnetic moments in Bohr magnetons are also indicated.

The most notable feature of these curves are the following :

(1) No signals corresponding to protons of thiourea were seen.

(2) The chemical shift increases with the concentration of the paramagnetic substance and has a tendency to become constant at higher concentrations. This saturation is more pronounced in the case of $Co(tu)_4Cl_2$. In each case the signal is very broad and at very high concentrations, it is so broad that it cannot be observed. (No attempt has been made to measure the line width.)

(3) At low concentration, in the case of water solution, the chemical shift falls smoothly but in acetone, there appears a kink in both the compounds. If the curve is extrapolated in the low concentration region, the zero chemical shift seems to occur at some finite concentration of the solute.

(4) The chemical shift in acetone solution is higher than that in water for the same concentration of the solute. In water solution, the chemical shift

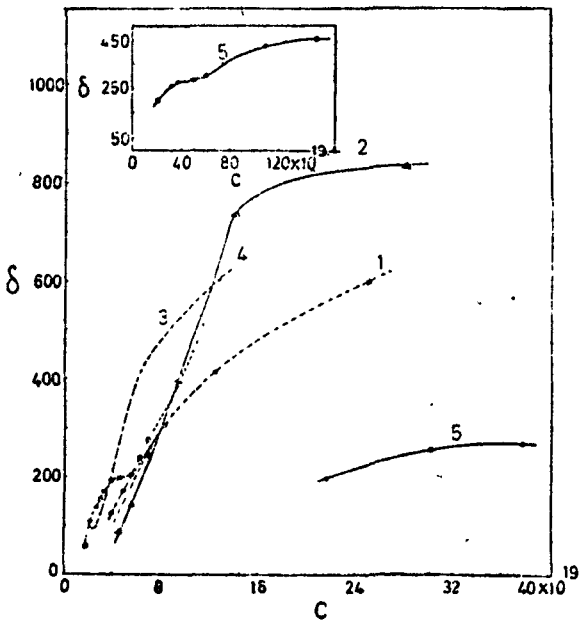

Fig. 1—Variation of chemical shift (δ) with concentration (number of the solute ions per c.c) *C* [Curve : 1. $=Co(tu)_4(NO_3)_2$ + water; 2. $Co(tu)_4Cl_2$ + water; 3. $Co(tu)_4(NO_3)_2$ + acetone; 4. $Co(tu)_4Cl_2$ + acetone; and 5. $CoCl_2 \cdot 6H_2O$ + water]

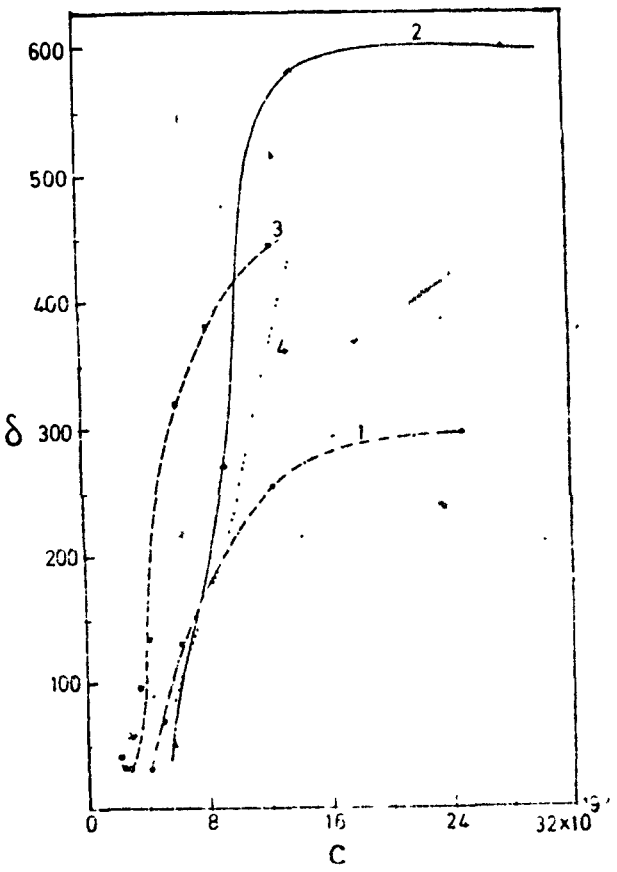

Fig. 2—Variation of chemical shift (δ) with concentration after applying bulk susceptibility correction

Curve	Solution	Magnetic moment Bohr magneton	Molar conductance Ω^{-1} cm^2
1.	$Co(tu)_4(NO_3)_2$ + water	4·4	91
2.	$Co(tu)_4Cl_2$ + water	4·0	160
3.	$Co(tu)_4(NO_3)_2$ + acetone	4·6	7·7
4.	$Co(tu)_4Cl_2$ + acetone	5·2	3·2

with $Co(tu)_4Cl_2$ is higher than with $Co(tu)_4(NO_3)_2$, but the reverse is the case in the acetone solution.

(5) For water solution, the chemical shift with $Co(tu)_4Cl_2$ is much higher than that with $CoCl_2 \cdot 6H_2O$.

(6) Chemical shift is up-field.

Each of the above observations can be explained on the following lines:

(1) The unpaired electron density in the coordinated thiourea protons is so great that the relaxation time is very much shortened and the signal is so much broadened as to be beyond experimental detection.

(2) It is known[4] that chemical shift is governed by the formula

$$\frac{\Delta H}{H} = \frac{8\pi}{3} \left| \psi(0) \right|^2 \frac{Z\chi}{n}$$

where $|\psi(0)|^2$ is the probability of the paramagnetic electrons to be at proton nucleus of the neighbouring solvent molecule, χ is the volume susceptibility, Z is the coordination number and n is the number of water molecules. Here we do not consider the contribution from the diamagnetic ions, i.e. Cl^- and NO_3^- to the chemical shift as their contributions to the chemical shift are very small[5]. For explaining our results we utilize the concept of iceberg formation around polar and non-polar solutes which goes on melting as the concentration is lowered[6]. It suggests that on diluting the solution, the Z value is lowered which results in the reduction of the chemical shift. The decrease in chemical shift is not explainable by changes in the measurable factor χ/n.

At higher concentration, the chemical shift tends to reach a constant value. This may be expected from the fact that at higher concentration, the water molecules ordinarily hydrated to a single ion at low concentration, are now shared by various ions. This effectively decreases Z. Again at still higher concentration, the spin-lattice relaxation times and the spin-exchange effect between cobalt ions contribute to the broadening of the signal beyond detection. By calculating the spin-lattice relaxation times of $Co(tu)_4Cl_2$ solution in water from the formula[7]

$$\frac{1}{T_1} = \frac{4\pi^2\gamma^2\eta N_p \mu^2_{eff}}{kT}$$

for the concentrations when signal is not observable, we obtain T_1 to be 0·00488 sec taking the viscosity of the solution to be equal to that of pure water. But viscosity of solution is apparently higher than that of pure water, therefore, T_1 is less than 0·00488 sec. It is difficult to observe the signal with this relaxation time. Similarly T_1 can be calculated in other cases also.

(3) The conductivity data show that the compounds are quite dissociated in water but slightly dissociated in acetone. At a low concentration in acetone solution, probably, extensive dissociation takes place and is responsible for showing kinks in the curve. In this region, one might expect that the formation of other types of compounds takes place. That the curves when extrapolated show that the chemical shift tends to zero, even if the concentration is not zero, indicates that at this concentration coordination number or hydration number tends to be zero.

(4) It can be said that as acetone has got a higher dipole moment than water and as in an ion-dipole system (here force depends upon the ionic charge and the dipole moment), acetone is more strongly attracted towards the ions than water and hence a greater overlap of the unpaired electron density at the acetone proton occurs. Moreover, acetone has molar refraction much higher than that of water, it is more polarizable and this results in higher chemical shift. In aqueous solution, $Co(tu)_4Cl_2$ dissociated more than $Co(tu)_4(NO_3)_2$ compound, as indicated by conductivity data. Now the ion-dipole interaction is more effective in shifting resonance peak than is the dipole-dipole interaction. Hence the chemical shift in case of $Co(tu)_4Cl_2$ should be more than that in the case of $Co(tu)_4(NO_3)_2$. In acetone the amount of dissociation may be just opposite to what we find in the aqueous solution, i.e. $Co(tu)_4(NO_3)_2$ is more dissociated than $Co(tu)_4Cl_2$. This is supported by conductivity data and may be responsible for the change in the nature of the chemical shift in the two solutions. From the magnetic moment measurements it appears that the more the dissociation, the less the magnetic moment, i.e. ionic species has less magnetic moment than the parent neutral molecule, which is quite probable.

(5) As the compounds are dissolved in water, they show pink colour and it is doubted that the replacement of thiourea by water takes place, which gives the characteristic pink colour of $[Co(H_2O)_6]^{2+}$ but the measurement of chemical shift eliminates this doubt. However, the rapid exchange between the thiourea and water molecules cannot be ruled out.

(6) The up-field shift indicates that the proton is better shielded which is quite expected since electron density increases on account of delocalized unpaired electrons.

The magnetic moments of all the samples correspond to three unpaired electrons and the structure seems to be tetrahedral with sp^3 hybridization. In undissociated molecules there is no hint to completely rule out the possibility of octahedral configuration with sp^3d^2 hybridization with 4 thiourea and two chlorine or nitrate ligands.

We have also undertaken the study of the EPR spectra of these compounds in solution phase to estimate the unpaired electron densities at various sites on the ligands.

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SHORT COMMUNICATION

Composition and stability of osmium(IV)–amino acids complexes

OMAR FAROOQ and NASEER AHMAD
Inorganic Research Laboratory, Chemistry Department, Aligarh Muslim University, Aligarh (India)
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The metal complexes of amino acids play very important roles in many biological systems. The interaction of transition metals with various amino acids has been extensively studied and the stabilities of the resulting complexes have been ascertained by several electrometric techniques[1–8]. Recently a programme of work to study the mode of binding of the transition metals of the platinum groups with certain amino acids and the determination of stabilities of their complexes has been undertaken by the authors[9–12]. The present communication deals with the interaction of osmium(IV) with some amino acids using sodium chloro-osmate in aqueous medium. pH-metric and potentiometric titrations were performed to calculate the successive equilibrium constants, overall stability constants and compositions. The values of ΔF^0 were computed from the relation, $-\Delta F^0 = RT \ln K_s$, where K_s = the overall stability constant.

Experimental

Sodium chloro-osmate (Johnson and Matthey, London) was used to prepare an aqueous solution whose strength was checked by the strychnine salt method[13]. The amino acids glycine, DL-α-alanine, β-alanine, DL-serine, L-proline, DL-methionine, DL-threonine, DL-taurine, DL-valine (biologically pure, B.D.H., England), L-asparagine, DL-phenylalanine and L-leucine (chromatographically pure, Merck, Germany) were employed and their standard solutions in twice-distilled air-free water were used in the titrations.

A Toshniwal titration potentiometer, model CLO6 (India) in conjunction with platinium and saturated calomel electrodes was used. A direct reading EIL pH-meter, model 23A (England) was employed with glass and calomel electrodes for pH-metric titrations. All titrations were performed in an oxygen-free atmosphere.

Results and discussion

A ratio of 1:4 (metal:amino acid) was established by potentiometric titrations for all the systems reported here. The stepwise successive constants or equilibrium constants were calculated by Bjerrum's[14] and Albert's[15] techniques. Three solutions: 50 ml of 0.01 *M* amino acid, 50 ml of 0.0025 *M* osmate and 50 ml containing 0.01 *M* amino acid and 0.0025 *M* osmate were separately titrated against 0.1 *M* standard carbonate-free potassium hydroxide. Only air-free con-

TABLE 1

OVERALL STABILITY CONSTANTS OF VARIOUS AMINO ACIDS–OSMATE SYSTEMS AT 28°C

Systems	*log (K_s/mol^2 l^{-2})*		*$-\Delta F^0$/kJ mol^{-1}*
	Calcd.	*Graphically*	
L-Asparagine–Na_2OsCl_6	5.17	5.20	3.10
DL-α-Alanine–Na_2OsCl_6	6.97	6.90	4.85
β-Alanine–Na_2OsCl_6	6.12	6.05	4.52
DL-α-Alanine–Na_2OsCl_6	5.58	5.60	4.31
Glycine–Na_2OsCl_6	5.04	5.60	4.35
DL-Isoleucine–Na_2OsCl_6	5.72	5.70	4.36
L-Leucine–Na_2OsCl_6	5.82	5.80	4.39
DL-Methionine[a]–Na_2OsCl_6	6.06	6.02	4.51
L-Proline–Na_2OsCl_6	7.02	7.00	4.89
DL-Serine–Na_2OsCl_6	5.60	5.50	4.18
DL-Taurine[a]–Na_2OsCl_6	6.00	6.05	4.49
DL-Threonine–Na_2OsCl_6	6.19	6.20	3.04
DL-Valine–Na_2OsCl_6	7.77	7.80	5.27

[a] Sulphur-containing amino acids.

ductivity water was used for dilution and in the titrations. The osmium concentration was maintained at 0.0025 *M*. The values of overall stability constants (K_s) are listed in Table 1.

In general, amino acids were found to produce complexes of high stability with metals. As the first stage of the reaction, one molecule of the amino acid combines with one atom of the metal producing a 1:1 complex species, MA^+. This species, however, did not combine promptly with another molecule of amino acid to produce the 1:2 complex species, MA_2^+. This equilibrium is only attained when the value of $\bar{n}$ (average number of molecules of amino acid which combine with one atom of metal) reaches 80% of the 1:1 complex. The value of $\bar{n}$ starts at nearly zero and reaches a maximum of approximately two. At this stage, the possibility of formation of MA_3^+ cannot be ruled out. Flood and Loars[16] agree with this analogy. When $\bar{n}=1$, the values of log K' and log K'' may be written as

$$\log K' = \log \bar{n} - \log(1-\bar{n}) - \log[\mathrm{Sc}]$$

$$\log K'' = \log(1-\bar{n}) - \log(2-\bar{n}) - \log[\mathrm{Sc}]$$

where [Sc] stands for the concentration of the complex-forming species and its value may be calculated by a simplified equation which holds good between pH 3 and 11 for simple amino-acid systems, namely,

$$\log[\mathrm{Sc}] = (\mathrm{pH} - \mathrm{p}K_a) + \log([\mathrm{HSc}^0] - [\mathrm{KOH}])$$

where $[HSc^0]$ is defined as the concentration of the free amino acid before the addition of the metal and [KOH] is the concentration of carbonate-free potassium hydroxide present in the solution after each gradual addition, if both the amino acid and metal are supposed to be absent. At the point where $\bar{n}=1$ (formation curve, $\bar{n}$ *vs.* $-\log[\mathrm{Sc}]$) the correct value for log[Sc] is obtained. The values of log K_s may

be written as $\log K_s = -2(-\log[Sc])$. The value of $\bar{n}$ is governed by the relation, $\bar{n} = 2[KOH]/[HSc^0]$ and $\log K_s$ is also equal to the logarithmic values of K' and K''. A few plots of $\bar{n}$ *vs.* $-\log[Sc]$ are given in Fig. 1.

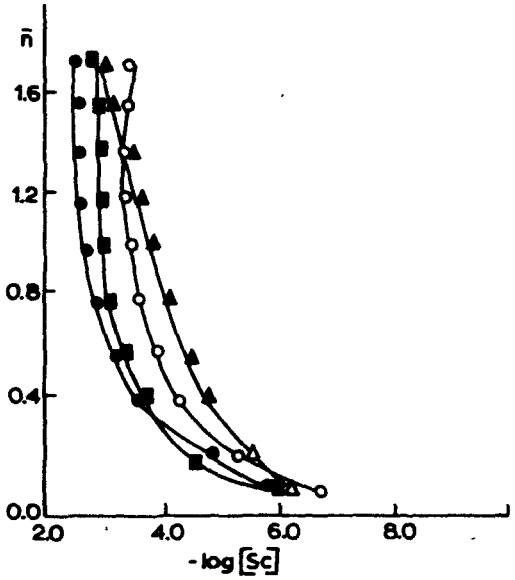

Fig. 1. Plots of $\bar{n}$ *vs.* $-\log[Sc]$, where [Sc] is the concentration of the complex-forming species. (●) Glycine–Na_2OsCl_6 system, (■) β-alanine–Na_2OsCl_6 system, (▲) DL-valine–Na_2OsCl_6 system, (○) L-proline–Na_2OsCl_6 system.

The values of $\log K_s$ calculated by applying the above relations are in good agreement with those obtained graphically. These values vary from 5.17 for L-asparagine to 7.77 for DL-valine, and the order of stability is: DL-valine > L-proline > DL-α-alanine > DL-threonine > β-alanine > DL-methionine > DL-taurine > L-leucine > DL-isoleucine > glycine > DL-serine > DL-phenylalanine > L-asparagine. There seems to be no relationship between the values of overall stability constants and the chain length or nature of the amino acid. Keeping in view the values of $\log K_s$ for various systems reported here, the following generalizations may be made.

(a) In the case of DL-α-alanine, β-alanine and DL-phenylalanine, the order of stability is: DL-α-alanine > β-alanine > DL-phenylalanine.

(b) The value of $\log K_s$ of L-leucine complex is slightly higher than the value of the DL-isoleucine complex.

(c) In the case of the sulphur-containing amino acids, the value of $\log K_s$ decreases as the distance between the amino and carboxylic group increases (between NH_2 and SO_2OH in case of DL-taurine). This does not justify the part played by the sulphur atom during complexation[6,9,10,17].

These values are lower than those of systems studied earlier[9–12] presumably due to the low avidity of osmium(IV) towards common amino acids. The actual nature of binding in these complexes is difficult to explain since the complex could not be isolated in a sufficiently pure state for analysis.

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SHORT COMMUNICATION

Stability and binding of Au(III) to certain amino acids using sodium chloroaurate

OMAR FAROOQ and NASEER AHMAD
Inorganic Research Laboratory, Chemistry Department, Aligarh Muslim University, Aligarh (India)
(Received 29th October 1973)

Complex formation between transition-metal ions and amino acids has been extensively examined by several experimental approaches[1–6]. A productive series of studies on metal–amino acid complex formation and stability was introduced by the paper of Albert[7] on the binding of several transition-metal ions by amino acids. Recently a detailed study on the binding of amino acids with transition metals having unusual valency states and metals belonging to the platinum group was undertaken by the authors[8–15]. The present study reports on the stabilities and binding of Au(II) with some amino acids using sodium chloroaurate. pH-metric and potentiometric titrations were performed to evaluate the overall stability constant and composition of a particular system. The relation, $\Delta F^0 = -RT \ln K_s$ was used to calculate the values of ΔF^0 at 25°C, where K_s = the overall stability constant.

Experimental

The amino acids, DL-α-alanine, β-alanine, glycine, DL-leucine, DL-methionine, L-proline, DL-serine, DL-threonine, DL-taurine, DL-valine (biologically pure, B.D.H., England), L-asparagine and DL-phenylalanine (chromatographically pure, Merck, Germany) were used and their standard solutions in water (air-free, twice-distilled) were employed in titrations. Sodium chloroaurate (Merck, pure product, Germany) was used. Gold was estimated gravimetrically[16].

The pH-metric titrations were performed with a direct reading EIL pH-meter, model 23A (England). A Toshniwal titration potentiometer, model CL06 (India) in conjunction with platinum and calomel electrodes, was used for potentiometric titrations. These studies were performed in an oxygen-free atmosphere at 25°C.

Results and discussion

The potentiometric titrations revealed a molar ratio of 1:3 (metal:amino acid) in all the systems reported herein. For each system, pH-metric titrations in triplicate were performed to calculate the stability constant in the order: (a) amino acid 0.01 *M*, (b) metal salt, 0.0033 *M* and (c) a mixture of sodium chloroaurate and amino acid having a total concentration of 0.0033 *M* and 0.01 *M*, respectively. Carbonate-free KOH was used as the titrant. The strength of the KOH solution was checked before each pH-metric titration. An appreciable inflection was found in the pH-metric titration indicating the association of amino acid with the metal ion.

In general, metal ion–ligand (amino acid) systems may be explained by considering the stepwise formation of complexes of varying composition, MA, MA_2, $MA_3 \ldots MA_n$, where M stands for the metal ion, A the ligand and n the maximum number of ligand molecules bound by the metal ion. The concentration of each complex species, at equilibrium is related to that of each of the other complexes by a series of expressions:

$$K_1 = [MA]/[M][A] \qquad K_2 = [MA_2]/[M][A] \qquad K_3 = [MA_3]/[M][A]$$
$$K_n = [MA_n]/[MA_{n-1}][A]$$

Here K_1, K_2, K_3, ..., K_n are successive association equilibrium constants; units of concentration are used for simplicity and convenience. The logarithm of the overall stability constant, log K_s would be the sum of the logarithms of the values of successive association constants:

$$\log K_s = \log K_1 + \log K_2 + \log K_3, \ldots, \log K_n$$

In the case of monoamino monocarboxylic acid (amino acid having two ionizing groups) the values may be written as,

$$K_1 = [MA^+]/[M][A^-] \qquad K_2 = [MA_2]/[MA^+][A^-] \qquad K_s = [MA_2]/[M][A^-]^2$$

During the process of complex formation, H^+ ions are formed, and the measurements of the concentration of these ions provide a method of checking the extent of complex formation. The values of successive constants may be written as,

$$K_1 = \bar{n}/(1-\bar{n})[Sc] \qquad K_2 = (\bar{n}-1)/(2-\bar{n})[Sc]$$

here [Sc] is the concentration of the coordinating species, and $\bar{n}$ is the average number of molecules of complex-forming agent bound by one atom of metal. The values of [Sc] may be calculated in pH range 3 to 11 from the relation given below

$$\log[Sc] = (pH - pK_a) + \log\{[HSc^0] - [KOH]\}$$

where $[HSc^0]$ is the initial concentration of amino acid before the addition of metal salt and [KOH] is the concentration of alkali when amino acid (complex forming agent) and metal are both absent. The values of $\bar{n}$ may be computed from the following simple relation.

$$\bar{n} = 2[KOH]/[HSc^0]$$

In the present study, the stability of the systems varies from L-proline (log $K_s = 10.84$) to DL-phenylalanine (log $K_s = 9.21$), and the order of stability may be written as: L-proline > glycine > β-alanine > DL-threonine > DL-methionine > DL-leucine > DL-α-alanine > DL-valine > DL-taurine > DL-serine > L-asparagine > DL-phenylalanine. The sulphur-containing amino acids, methionine and taurine appeared to behave like the simple monoamino monocarboxylic acids. In the case of DL-methionine, $CH_3SCH_2CH_2(NH_2)COOH$, the thio-ether sulphur contributed little to the stability of the complex. On the other hand taurine, a sulphonic acid, did not show any specific affinity for the Au^{3+} ion. But it may safely be said in the case of sulphur containing amino acids, that the value of log K_s decreases as

the distance between the amino and carboxylic groups increases or the distance between the NH_2 and SO_2OH groups in the case of taurine[10]. The present studies do not throw any light on the part played by sulphur atoms These values are higher than those in the systems studied earlier[8–11], but are of lower magnitude than Cu^{2+} and Pd^{2+} systems[13] indicating thereby the high affinity of Au^{3+} for amino acids Copper and gold show a strong tendency to form coordination complexes

The values of -2 log [Sc] at $\bar{n}=1$, correspond to the value of log K_1 for a particular system, while in the previous studies[7–10] it was observed that log K_s was equal to -2 log[Sc] It is most probably due to the formation of polynuclear compounds The monohydroxides of coinage metals tend to associate in solution to form polynuclear complexes This phenomenon will occur in a region of pH somewhat below the point at which the metal hydroxide begins to precipitate

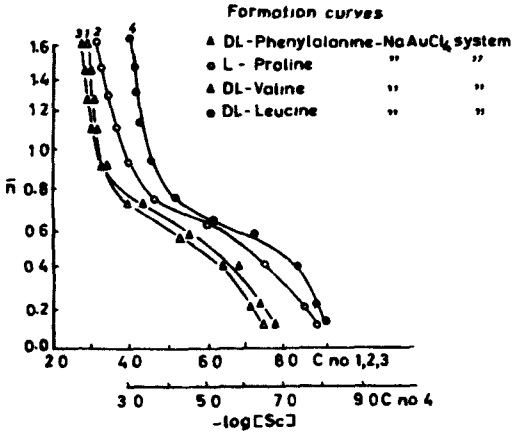

Fig 1 Plots of $\bar{n}$ *vs* $-\log[Sc]$, where [Sc] is the concentration of (△) DL-phenylalanine, (○) L-proline, (▲) DL-valine, (●) DL-leucine

TABLE 1

VALUES OF EQUILIBRIUM AND OVERALL STABILITY CONSTANTS FOR VARIOUS SODIUM CHLOROAURATE–AMINO ACID SYSTEMS AT 25°C

Systems	*log* K_1	*log* K_2	*log* $(K_s/l^2\ mol^{-2})$	$-\Delta F^0$/*kcal mol*$^{-1}$
DL-α-Alanine–$NaAuCl_4$	6 92	3 04	9 96	135 4
β-Alanine–$NaAuCl_4$	6 85	3 61	10 46	144 9
L-Asparagine–$NaAuCl_4$	6 18	3 10	9 28	126 1
Glycine–$NaAuCl_4$	7 05	3 52	10 57	143 5
DL-Leucine–$NaAuCl_4$	7 14	3 04	10 18	138 3
DL-Methionine–$NaAuCl_4$	7 23	2 96	10 19	138 5
DL-Phenylalanine–$NaAuCl_4$	6 46	2 75	9 21	125 1
L-Proline–$NaAuCl_4$	7 85	2 99	10 84	147 3
DL-Serine–$NaAuCl_4$	6 54	2 79	9 34	126 9
DL-Threonine–$NaAuCl_4$	6 74	3 45	10 19	138 5
DL-Taurine–$NaAuCl_4$	6 55	2 91	9 46	128 5
DL-Valine–$NaAuCl_4$	6 80	3 05	9 85	134 0

In the crystalline hydroxides of these metals, two types of linkages between metal atoms are found: partially covalent oxygen bridges of the type, M–O–M and hydroxyl bridges of the type, M–O–H–O–M[17]. Probably both types of bonds are effective in the formation of polynuclear complexes. Mattock[18] has pointed out that the metals which tend to form polynuclear complexes, are those which form metal–oxygen bonds with comparable amounts of ionic and covalent character. $Au(OH)_3$ is produced when $AuCl_3$ reacts with alkali. Auric hydroxide is soluble in excess of alkali and may produce the stable aurate, $KAuO_2$. This position is attained when the pH reaches ~8.0. Therefore, the calculated values of log K_s deviated a lot from the values obtained by plotting $\bar{n}$ *vs.* $-\log[Sc]$ at $\bar{n}=1$. The values of log K_1, log K_2, log K_s and ΔF^0 are given in Table 1. A few formation curves ($\bar{n}$ *vs.* $-\log[Sc]$) are given in Fig. 1. The real nature of bonding in these complexes is a matter of speculation and needs support from several experimental approaches.

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SHORT COMMUNICATION

Stability and stepwise association of rhodium(III) chloride with some amino acids

OMAR FAROOQ and NASEER AHMAD
Inorganic Research Laboratory, Chemistry Department, Aligarh Muslim University, Aligarh U.P. (India)
(Received 9th July 1974)

Owing to the biological importance of amino acids and their related compounds, appreciable attention has been paid to the stability of transition-metal complexes with amino acids[1–4]. Recent work in this laboratory on the mode of interaction of various amino acids with transition metals and with several platinum group metals has shown the likelihood of association of these metals with certain common amino acids including sulphur containing amino acids[5–15]. The present communication deals with the results of composition and stability of certain amino acid complexes with trivalent rhodium. The studies are mainly based upon the pH-metric titration method in aqueous medium as suggested by Bjerrum[16] and modified by Albert[17]. Potentiometric titrations were performed for each reported system herein. The relation, $-\Delta F^0 = RT \ln K_v$ (where K_v = overall stability constant) was employed to compute the values of ΔF^0 at 27°C. All studies were done under anaerobic conditions and in an oxygen-free atmosphere.

Experimental

The amino acids, glycine, DL-α-alanine, β-alanine, L-leucine, L-proline, DL-serine, DL-taurine, DL-methionine, DL-valine (B.D.H., biologically pure), L-asparagine, DL-phenylalanine, DL-isoleucine and DL-threonine (E. Merck, chromatographically pure) were used and their solutions were prepared in twice distilled air-free water. Rhodium chloride (Johnson Matthey, England) in aqueous solution was estimated gravimetrically[18].

A Toshniwal titration potentiometer; model CL06 (India), in conjunction with platinum and calomel electrodes, was employed for potentiometric studies, whilst an EIL, Direct Reading pH-meter, model 23A (England) was used for pH-metric measurements. Glass and saturated calomel electrodes were used as indicator and reference electrodes, respectively. Carbonate-free KOH was used as the titrant. The solution was stored in a Pyrex bottle fitted with a guard tube containing anhydrous KOH to avoid atmospheric carbon dioxide. The strength was checked before titrating each set of samples.

Results and discussion

A stoichiometric ratio of 1:3 (metal:amino acid) was observed by potentiometric titrations in all the systems reported herein. pH-metric titrations in tri-

plicate were performed to evaluate the successive equilibrium constants (K_1 and K_2) and the overall stability constant (K_3) in the order (a) amino acid 0.01 *M* (b) rhodium chloride 0.0033 *M* and (c) a mixture of rhodium chloride and amino acid having a total concentration of 0.0033 *M* and 0.01 *M*, respectively. Rhodium being trivalent, the concentration was kept to 0.0033 *M* in all the systems. The values of partial or successive stability constants (log K_1 and log K_2) and the overall stability constants are listed in Table 1.

TABLE 1

VALUES OF SUCCESSIVE EQUILIBRIUM AND OVERALL STABILITY CONSTANTS FOR VARIOUS RHODIUM(III) CHLORIDE–AMINO ACID SYSTEMS AT 25°C

System	*log* K_1	*log* K_2	*log* (K_3/*mol*$^{-2}$ *l*^{2})	$-\Delta H^0$ *kcal mol*
DL-α-Alanine $RhCl_3$	7.19	3.09	10.28	14.1
β-Alanine $RhCl_3$	6.63	3.29	9.92	13.6
L-Asparagine $RhCl_3$	6.86	2.87	9.73	13.4
Glycine $RhCl_3$	7.34	3.03	10.37	14.2
DL-Isoleucine $RhCl_3$	7.16	2.76	9.92	13.6
L-Leucine $RhCl_3$	7.13	2.79	10.10	13.9
DL-Methionine[a] $RhCl_3$	6.69	2.69	9.38	12.9
DL-Phenylalanine $RhCl_3$	6.82	3.12	9.94	13.7
L-Proline $RhCl_3$	8.24	3.00	11.24	15.4
DL-Serine $RhCl_3$	6.92	3.03	9.95	13.7
DL-Taurine[a] $RhCl_3$	6.61	2.68	9.29	12.7
DL-Threonine $RhCl_3$	6.86	3.02	9.88	13.6
DL-Valine $RhCl_3$	7.14	2.66	9.80	13.5

[a] Sulphur containing amino acids

In general, the majority of the amino acids exhibited the same binding sequence as that observed in various other systems. Amino acids produce complexes of high stability with metals. Monoaminomonocarboxylic acids, amino acids having two ionizing groups, combine with one atom of the metal to produce a 1:1 species MA^{2+} at the initial stage of the reaction. Another molecule of the amino acid probably does not coordinate with this species to produce a more complex species MA_2^{+}. An equilibrium is attained and the value of n (average number of complex forming agent amino acid, bound by one atom of the metal) reaches 80% of the dominating species, MA^{+} of 1:1 complex. The value of $\bar{n}$ starts at zero and reaches a maximum of approximately two. Flood and Loars[19] suggested that the probability of formation of MA_3^{+} species may not be totally ruled out at this stage of the reaction, and the plot of n vs. $-\log$ [Sc] where [Sc] stands for the concentration of the complex forming species, shows some abnormality.

The concentration of various species at equilibrium is directly linked by a series of expressions to that of each of the other complexes at equilibrium.

$$K_1 = [MA^{+}]/[M][A],\ K_2 = [MA_2^{+}]/[M][A],\ K_3 = [MA_3^{+}]/[M][A]$$
$$K_n = [MA_n]/[MA_{n-1}][A]$$

K_1, K_2, K_3 ... K_n are termed as partial stability, successive association or equili

brium constants. The algebraic sum of the logarithmic values of these constants is defined as the overall stability constant, log K_s and may be represented as log $K_s = \log K_1 + \log K_2 + \log K_3 + \ldots \ldots + \log K_n$. In the present study, the value of K_s may be rewritten as,

$$\log K_s = \log K_1 + \log K_2 \text{ or } \log K_s = \log [MA_2]/[M][A^-]^2$$

As the complex formation starts, hydrogen ions are liberated and the pH of the esulting mixture can be used to check the extent of complex formation in the olution phase. When the value of $\bar{n}$ reaches nearly 1, the values of successive ssociation constants, K_1 and K_2 may be expressed as

$$\log K_1 = \log \bar{n} - \log (1-\bar{n}) - \log [Sc];$$
$$\log K_2 = \log (\bar{n}-1) - \log (2-\bar{n}) - \log [Sc].$$

Sc] may be evaluated by a simplified equation in the pH-range 3 to 11, *viz.*,

$$\log [Sc] = (pH - pK_a) + \log ([HSc^0] - [KOH]).$$

ere $[HSc^0]$ and [KOH] represent the initial concentration of amino acid before he addition of the metal salt and the concentration of titrant when complex orming agent and metal salt were both absent, respectively. The values of $\bar{n}$ rom 0 to 2 were computed from the relation, $\bar{n} = 2[KOH]/[HSc^0]$.

The values of the overall stability constants, log K_s, vary from 9.25 L-asparagine) to 11.24 in L-proline and the general order of stabilities is: -proline > glycine > DL-α-alanine > L-leucine > DL-serine ≥ DL-phenylalanine > β-alanine = DL-isoleucine > DL-threonine > DL-valine > L-asparagine > DL-nethionine > DL-taurine. Undoubtedly, sulphur-containing amino acids (DL-nethionine and DL-taurine) appear to behave like a monoaminomonocarboxylic cid. Veidis and Palenik[20] established that thio-ether type sulphur in methionine, $CH_3SCH_2CH_2(NH_2)COOH$, contributed very little to the stability of its complexes. Similarly, taurine, a sulphonic amino acid, did not show any specific preference or rhodium. These values are somewhat higher than the values of other systems tudied earlier, showing thereby the high affinity of rhodium(III) chloride for amino cid[5-12].

The plots of $\bar{n}$ *vs.* $-\log$ [Sc] (formation curves) correspond to the value of log K_1 when $\bar{n} = 1$ for a particular system. Similar behaviour was observed in he case of Au^{3+}–amino acid systems[13]. On the other hand in most of the previous tudies it was noticed that the value of log K_s was equal to -2 log [Sc] t $\bar{n} = 1$. The possibility of formation of polynuclear compounds cannot be totally uled out. The hydroxides of heavy and coinage metals associate themselves to roduce polynuclear adducts in solution phase when the pH of the system approaches he region at which MOH is precipitated. Two common types of linkages are eported between metal atoms in crystalline hydroxides[21]: M–O–M partially ovalent oxygen bridges and hydroxyl bridges of the type, M–O–H–M. Most robably both types of linkages are involved in the formation of polynuclear omplexes.

. In the present study, the values of log K_s deviated a lot from the other ystems but they are similar in magnitude to the values of Au^{3+}–amino acid ystems reported earlier[13]. Some curves of $\bar{n}$ against $-\log$ [Sc] are given in Fig. 1

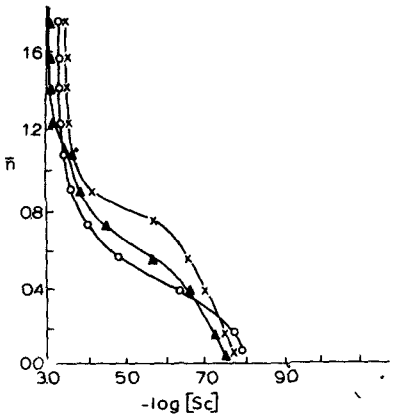

Fig 1 Formation curves $\bar{n}$ *vs* $-\log$ [Sc] (○) DL-valine–$RhCl_3$ system, (▲) L-asparagine–$RhCl_3$ system, (×) DL-α-alanine–$RhCl_3$ system

which support this claim. It is difficult to assign a definite general structure to these complexes since they could not be isolated in the pure state.

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METAL-AMINO ACID INTERACTION, I

A STUDY OF THE COMPLEX COMPOUNDS OF TRIVALENT RARE EARTHS WITH L-ASPARTIC ACID

OMAR FAROOQ, ANEES UDDIN MALIK* and NASEER AHMAD

(Inorganic Research Laboratory, Chemistry Department, Aligarh Muslim University, Aligarh U.P. India)

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A number of transition metal and inner transition metal complexes with α-amino acids have been studied mostly in solutions employing certain physicochemical techniques [1—10]. From the literature it appears that very limited attention has been paid to the isolation and elucidation of the structure of rare earth complexes with amino acids. The present communication deals with the interaction of L-aspartic acid with trivalent rare earth ions (Y, La, Ce—Lu except Pm). The complexes have been isolated and identified by IR, magnetic measurement, thermogravimetric analysis, molar conductance and elemental analysis.

Experimental

Freshly prepared rare earth carbonates were treated with L-aspartic acid in stoichiometric proportions in aqueous solution. The mixture was stirred, filtered and concentrated, mixed with dehydrated alcohol and allowed to evaporate slowly in vacuum at room temperature.

The complexes were analysed for C, H and N, by the Microanalytical Service, I.I.T. Kanpur (India) and rare earths were estimated as oxalates [11]. The IR spectra were taken on a Beckman Spectrophotometer model BK-56 in the range 2.5 to 16 in KBr pellets. Thermogravimetric analysis were performed on a Stanton thermobalance (London) between 25 and 600°C with a heating rate of 6°C per minute in air. Molar conductances were recorded by using a Philips conductivity bridge model PR 9500 in conjunction with a dip type cell (cell factor 1.48) and magnetic measurements were carried out at 27°C employing Faraday's method. Rare earth oxides were purchased from KOCH-Light (London). These compounds are highly hygroscopic and do not dissolve in common organic solvents, have high solubity in water. No melting is observed up to 360°C. Table I gives the characteristic data of these complexes.

Results and discussion

Elemental analyses and TGA studies exhibit the formula $M(Asp\text{-}H)_3 \cdot 3\ H_2O$ where M stands for Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. The removal of water at 120—160°C (10—12% wt. loss) confirms that all molecules are co-ordinated to metal ions and are not just water of crystallization [12]. The partially dehydrated compounds are stable up to 230°C and then decomposition sets in. Most probably CO and CO_2 are pro-

* Department of Metallurgy and Material Science. University of Liverpool, Liverpool, England.

Table I

Complexes prepared in this study and some characteristic data

Complex	Colour	C		H		N		Metal		Magnetic moment (BM)	Molar cond. in mhos
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found		
$Y(Asp)_3 3H_2O$	White	26.70	26.62	4.45	4.27	7.78	7.75	16.48	16.42	Diamag	0.31
$La(Asp)_3 3H_2O$	White	24.44	24.38	4.07	4.10	7.13	6.89	23.58	23.54	Diamag	0.31
$Ce(Asp)_3 3H_2O$	Rosy pink	24.39	24.65	4.06	4.16	7.11	7.16	23.71	23.81	2.5	8.30
$Pr(Asp)_3 3H_2O$	Yellowish areen	24.35	24.25	4.06	4.18	7.12	7.07	23.83	23.90	3.5	0.30
$Nd(Asp)_3 3H_2O$	Pink	24.22	25.00	4.04	4.01	7.23	7.15	24.30	24.50	3.8	0.30
$Sm(Asp)_3 3H_2O$	White	23.96	23.87	3.99	3.95	6.99	6.92	23.36	23.42	2.0	0.30
$Eu(Asp)_3 3H_2O$	White	23.91	24.00	3.98	3.96	6.97	6.99	25.26	25.32	3.4	0.32
$Gd(Asp)_3 3H_2O$	White	23.70	23.94	3.95	4.05	6.91	7.29	25.89	26.02	7.8	0.31
$Tb(Asp)_3 3H_2O$	White	23.64	24.28	3.94	4.43	6.89	7.28	26.09	26.12	—	0.32
$Dy(Asp)_3 3H_2O$	Dirty white	23.51	24.61	3.92	4.02	6.86	6.84	26.59	26.55	9.8	0.32
$Ho(Asp)_3 3H_2O$	Dirty white	23.41	23.30	3.97	4.04	6.79	6.77	26.80	26.98	10.7	0.31
$Er(Asp)_3 3H_2O$	White	23.24	23.20	3.85	3.97	6.84	6.80	27.00	27.10	9.7	0.32
$Tm(Asp)_3 3H_2O$	White	23.08	23.20	3.84	3.75	6.78	6.75	27.20	27.90	6.8	0.32
$Yb(Asp)_3 3H_2O$	White	23.05	23.00	3.84	3.76	6.76	6.71	27.70	27.40	4.6	0.32
$Lu(Asp)_3 3H_2O$	White	23.03	23.10	3.84	3.88	6.72	6.70	28.13	28.20	Diamag	0.31

Asp = L-aspartic acid; $H = (C_4H_6O_4N)$

duced at 350 700°C leading to the formation of stable oxides. Ce(III) complex deviated from this behaviour and there is direct formation of CeO_2 from 340 °C onwards with a weight loss of about 70%.

The usual unequal double humped curve is obtained on plotting magnetic values in B. M. against atomic number [13]. The molar conductances of 2×10^{-1} *M* aqueous solution are of the order of 0.21 ± 0.01 mhos, but the corresponding trichlorides have about 2.8 times higher values then these complexes. These larger values of the rare earth halides might be due to the high ionic mobility of the halide ions as compared to those of large amino acid anions.

The bands which throw some light on the co-ordinating properties of amino acids are: NH_3^+ sym. asym [14], COO^- sym COO^- asym [15] CN stretchings and two unassigned medium intensity characteristic bands at 2060 and 1905 of L-aspartic acid [17]. The NH_3^+ asym stretchings of free aspartic acid appear as medium intensity bands at 1610 and 1510 cm^{-1}, respectively. The position of these bands remains unaltered on complexation, whereas a slight increase of 10– 25 cm^{-1} in the sym vibrations is observed. The COO^- sym vibration (1420 cm^{-1}s) present in the free acid is lowered by 20—25 cm^{-1} and the COO^- asym (1640 cm^{-1} m) is reduced by 5 –10 cm^{-1} only on complexation. The CN stretching band of medium intensity at 935 cm^{-1} in L-aspartic acid showed a lowering of 20 40 cm^{-1} on complex formation. Usually in amino acids, co-ordination takes place through the carboxylic group with consequent change in the position of NH_3^+ stretchings [18]. The presence of co-ordinated water is revealed by the presence of a medium intensity OH stretching band near 3400 cm^{-1} and OH rocking vibrations of strong intensity at 850 cm^{-1} [19, 20]. The exceptional bands of L-aspartic acid disappear on complexation.

Hence the formation of rare earth complexes is achieved through the displacement of the proton of the —COOH group by the rare earth ions. Moreover, aspartic acid (H_2L) is expected to loose a proton from —COOH (pK_a ~4) rather than from NH_3^+ (pK_a ~9.8) and the low affinity of lanthanide cations for NH_2 is unlikely to, in effect, reverse this order of acidities. It may be concluded that zwitter ion character of L-aspartic acid retained on complexation and that the possibility of co-ordination through nitrogen is ruled out.

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OMAR FAROOQ
ANEES UDDIN MALIK
NASEER AHMAD
Inorganic Research Laboratory, Chemistry Department, Aligarh Muslim University, A.M.U. Aligarh (U.P.) India.

30/LANTHANIDE COMPLEXES OF THIOGLYCOLIC ACID

OMAR FAROOQ, ANEES UDDIN MALIK (°) and NASEER AHMAD
Inorganic Research Laboratory, Chemistry Department, Aligarh Muslim University, Aligarh, U.P., India

Summary. — Some hydrated lanthanide complexes of general formula $M(L)_3(H_2O)_4$ with thioglycolic acid (HL) have been synthesised and their physical properties investigated. The magnetic data show characteristic unequal double humped curve. Thermogravimetric analyses show that probably all the water molecules are coordinated to the metal ion. The IR spectra show that these metals are bonded to the carboxylic group of the acid through the release of a proton. Molar conductances in aqueous solution of the same magnitude as those of the simple metal salt, highly melting nature and insolubility in common organic solvents support this suggestion.

Riassunto. — Vengono riportati complessi idrati di lantanidi con acido tioglicolico (HL), di formula generale $M(L)_3(H_2O)_4$. I momenti magnetici presentano la caratteristica curva a doppio massimo. Le analisi termogravimetriche stanno ad indicare che le molecole di acqua sono legate allo ione metallico; gli spettri IR sono in accordo con una struttura avente il legante coordinato tramite il gruppo tiocarbossilato. Le conducibilità molari in soluzione acquosa, gli alti punti di fusione e l'insolubilità nei comuni solventi organici sono in accordo con tale ipotesi.

Thioacids play a vital role in many biological systems, and their metal complexes have been extensively studied. The complexes of thioglycolic acid with various metals are reported in the literature and Ohashi and co-workers have recently described the complexation of some transition metals with thioglycolic and substituted thioglycolic acids ([1-4]). However, no systematic attempt has yet been made to study the mode of bonding of sulphur-containing acids to lanthanides. The pre-

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(°) Present address: Department of Metallurgy and Material Science, Liverpool University, Liverpool England.

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sent communication deals with the syntheses and properties of rare earth complexes of thioglycolic acid (hereafter HL) with the aim of deducing the nature of bonding of these ligands.

EXPERIMENTAL

MATERIALS

Rare earth oxides (Ce to Lu except Pm, Y and La) were « Johnson Matthey » spectroscopically pure products. Thioglycolic acid was « E. Merck », pro analysis grade reagent.

PREPARATION OF LANTHANIDE THIOGLYCOLATES

A freshly prepared solution of a slight excess of rare earth carbonate in air-free double-distilled water was mixed with thioglycolic acid. The mixture was stirred vigorously and excess carbonate removed by centrifugation. The solution was concentrated and the compound obtained in crude form by adding absolute ethanol. The crude mass was washed several times with a small quantity of cold water, ethanol and, finally, ether. The complexes were dried over P_2O_5 *in vacuo*.

INSTRUMENTS

IR spectra in the range 2500 to 16000 nm were recorded on KBr pellets with a « Perkin-Elmer » *Infracord* 137B spectrophotometer. The far-IR spectra were recorded on Cs plates with a « Beckman » BK 56 spectrophotometer using Nujol as mulling agent. Thermogravimetric analyses were run on a « Stanton Redcroft » TG-750, thermobalance in the range 25-900 °C at a heating rate of 6 °C/min. Molar conductances were measured with a « Philips » conductivity bridge PR 9500 and a dip type cell (cell factor 1.33 cm^{-1}). Magnetic measurements were made by the Faraday method using a Cahn 7600 system modified by using a Cahn GRAM-balance. The calibrant was mercury tetrathiocyanatocobaltate(II). Elemental analyses were performed by the Microanalytical Service, I.I.T., Kanpur (India). The rare-earths were estimated as their oxalates (5).

RESULTS AND DISCUSSION

Elemental and thermogravimetric analyses, and the other related studies show that all of the compounds can be represented by the general formula $M(L)_3(H_2O)_3$. Thermograms show that dehydration occurs in the temperature range 120-200 °C and that oxides begin to form at *ca.* 850 °C. The cerium(III) thioglycolate trihydrate deviated considerably from this general behaviour, and the formation of CeO_2 began at *ca.* 400 °C. The removal of three water molecules at 120-200 °C indicates that the water molecules are coordinated to the metal ions (6).

Thioglycolic acid can coordinate through oxygen of the carboxylic group, through the sulphur atom, or through both. There is also a possibility of bridging to form polynuclear complexes. It is a well established fact that under normal con-

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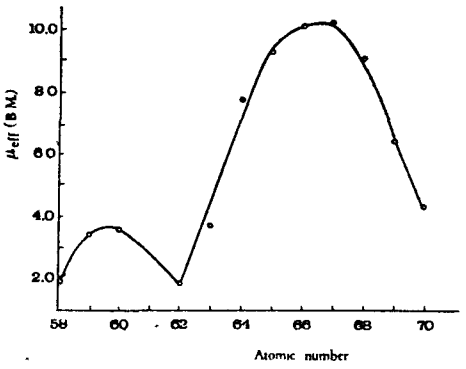
ditions thioether sulphur does not coordinate with metal ions. For instance the possibility of coordination through sulphur in methionine, a sulphur-containing amino acid, is almost ruled out in its metal complexes ([7]).

When plotted against the atomic number of the rare earths the magnetic moment, μ_{eff}, calculated after applying a diamagnetic correction for the ligand, produced the characteristic unequal double humped curve ([8]) (see figure). The molar conductances of 10^{-3} *M* aqueous solutions of rare-earth thioglycolates are of the order of 1.65 ± 0.01 ohm^{-1} cm^2 mole^{-1} at 25 °C and those of corresponding trihalides of rare-earths of *ca.* the same order but about 2.8 times higher than those of the correspoding thioglycolates. This may be due to the high ionic mobility of the chloride ions as compared to that of the large thioacid anion. Since the three water molecules are coordinated, it is probable that the thioglycolic acid acts as a unidentate ligand. Three bidentate thioglycolic ligands would raise the coordination number of the lanthanide ions to nine, which is impossible. In addition this would have resulted in considerable lowering of the molar conductances of the complexes as compared with those of the corresponding rare-earth salts.



The IR spectra of these complexes in the 700-1600 cm^{-1} region, gives insight into the coordination in these complexes. The assignments, which are based upon the previous studies on thio and carboxylate complexes ([9-13]), are listed in table 2. The bands expected to be affected by coordination are $\nu(COO)_{sym}$ and $\nu(COO)_{asym}$, and *M*—O, C—S and S—H stretching vibrations. The strong bands at 1710 and 1390 cm^{-1} are assigned to $\nu(COO)_{asym}$ and $\nu(COO)_{sym}$ vibrations, respectively, in the free ligand. These bands are those most affected by coordination and appear at 1562 and 1408 cm^{-1}, with the same intensity, in these compounds. A band of variable intensity (weak to medium) at *ca.* 450 cm^{-1} may be assigned to *M*—O stretch-

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TABLE 1. — SOME CHARACTERISING DATA

Complex	C, %		H, %		*M*, %		μ_{eff} (B.M.)	Molar conductance (ohm^{-1} cm^2 $mole^{-1}$)	Colour
	calcd	found	calcd	found	calcd	found			
$Y(L)_3(H_2O)_3$	17.29	17.20	3.62	3.70	21.35	21.40	Diamag.	1.64	Light yellow
$La(L)_3(H_2O)_3$	15.44	15.40	3.21	3.18	29.81	29.75	Diamag.	1.66	Dirty white
$Ce(L)_3(H_2O)_3$	15.47	15.40	3.20	3.17	29.83	29.86	1.93	1.66	Light pink
$Pr(L)_3(H_2O)_3$	15.37	15.32	3.19	3.22	30.90	30.98	3.40	1.66	Light yellow
$Nd(L)_3(H_2O)_3$	15.26	15.30	3.18	3.20	30.58	30.62	3.52	1.66	Pinkish White
$Sm(L)_3(H_2O)_3$	10.07	15.15	3.14	3.10	31.47	31.50	1.88	1.66	Dirty white
$Lu(L)_3(H_2O)_3$	15.02	15.00	3.12	3.20	31.60	31.60	3.68	1.66	Dirty white
$Gd(L)_3(H_2O)_3$	14.85	14.90	3.09	3.20	32.44	32.62	7.75	1.65	Dirty white
$Tb(L)_3(H_2O)_3$	14.80	14.90	3.08	3.00	32.55	32.60	9.30	1.65	Dirty white
$Dy(L)_3(H_2O)_3$	14.64	14.70	3.06	3.01	33.17	33.25	10.05	1.65	Dirty white
$Ho(L)_3(H_2O)_3$	14.62	14.72	3.04	3.12	33.50	33.70	10.18	1.66	White
$Er(L)_3(H_2O)_3$	14.56	14.60	3.03	3.09	33.81	33.85	9.10	1.64	White
$Tm(L)_3(H_2O)_3$	14.50	14.60	3.02	3.07	34.03	34.30	7.42	1.64	White
$Yb(L)_3(H_2O)_3$	14.38	14.40	2.99	3.01	34.58	34.62	4.35	1.64	White
$Lu(L)_3(H_2O)_3$	14.33	14.39	2.98	2.92	34.83	34.90	Diamag.	1.64	Dull white

TABLE 2. — INFRARED SPECTRAL FREQUENCIES (cm^{-1}) OF $M(L)_3(H_2O)_3$ COMPLEXES AND THIOGLYCOLIC ACID (*)

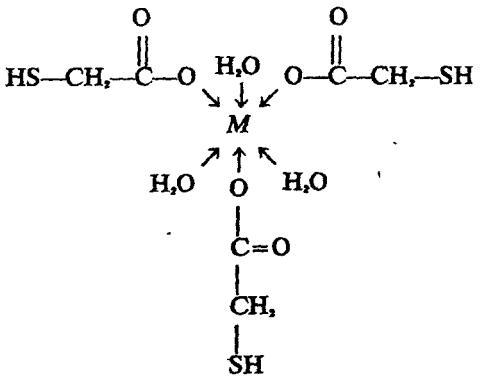
M/*HL*	$\nu(COO)_{asym}$	$\nu(COO)_{sym}$	ν(S—H)	ν(O—H)	ρ(OH)	ν(M—O)
HL	1710 *vs*	1390 *ms*	2564 *w*			
Y	1562 *s*	1408 *vs*		3545 *m*	930 *m*	452 *w*
La	1563 *s*	1408 *s*		3550 *m*	920 *m*	450 *m*
Ce	1562 *s*	1408 *s*		3500 *m*	935 *m*	450 *mb*
Pr	1562 *ms*	1400 *vs*		3550 *m*	940 *m*	452 *m*
Nd	1560 *s*	1400 *s*		3550 *m*	930 *m*	450 *w*
Sm	1562 *vs*	1408 *m*		3500 *mb*	935 *m*	452 *w*
Eu	1562 *vs*	1408 *s*		3545 *m*	450 *m*	450 *w*
Gd	1562 *s*	1408 *ms*		3550 *m*	890 *mb*	452 *w*
Tb	1564 *s*	1408 *s*		3550 *m*	940 *m*	450 *w*
Dy	1564 *vs*	1408 *s*		3545 *mb*	890 *m*	450 *m*
Ho	1562 *m*	1408 *ms*		3500 *mb*	940 *m*	454 *w*
Er	1562 *m*	1408 *m*		3550 *m*	940 *m*	450 *m*
Tm	1562 *vs*	1408 *s*		3550 *mb*	940 *m*	452 *w*
Yb	1562 *s*	1405 *s*		3550 *mb*	945 *m*	452 *w*
Lu	1560 *s*	1408 *ms*		3545 *m*	940 *m*	450 *w*

(*) *vs* = very strong; *s* = strong; *ms* = medium and sharp; *m* = medium; *mb* = medium and broad; *w* = weak.

ing ([13]). The C—S stretching vibration appears as a band of weak intensity in the range 700-600 cm^{-1}, but remains unaffected in both intensity and position on coordination. ν(S—H) appears as a weak band in the range 2600-2550 cm^{-1} and is quite difficult to locate in samples examined as thin films and is obscured in complexes having a carboxylic group. No definite change in intensity or shift in energy is observed. The bands of medium intensity at 3550 and at *ca.* 940 and 890 cm^{-1} are ν(O—H) and rocking vibrational modes of coordinated water, respectively, in the compounds ([14]).

([14]) P. J. Lucchesi, W. A. Glasson, *J. Amer. Chem. Soc.*, **78**, 1347 (1956); ref. (*), p. 156.

The thermograms, molar conductances and IR spectra lead to the conclusion tha coordination of thioglycolate ion occurs *via* the oxygen of the carboxylic group b the release of proton from the acid and not through sulphur. The structure of thes complexes is believed to be:



M = trivalent rare-earth ion.

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Complexes of Nitroalizarin with Zn(II), Mn(II), Co(II), Ni(II) & Y(III)

S. M. F. Rahman, Naseer Ahmad & Vijay Kumar
Department of Chemistry, Aligarh Muslim University, Aligarh

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3-Nitroalizarin forms 1 : 1 complexes with divalent zinc, manganese, cobalt, nickel and trivalent yttrium. The apparent formation constants of these complexes have been evaluated by Job's and molar ratio methods. The 1 : 1 stoichiometry for the complexes is supported by elemental analysis of the solid complexes. TGA data indicate that the water is coordinated. Molar conductance in dimethyl sulphoxide show them to be non-electrolytes. IR data show that the chelation with the ligand occurs at C_1-OH and the oxygen of C_9-CO group.

GEYER and Smith[1], Kiel and Heertjes[2], and Ahmad *et al.*[3] have studied the complexes of Cu, a few pairs of metals such as Ca-Al, Ca-Fe, Ca-Cr, Ba-Al, Sn-Al, Na-Al, K-Al and of rare earths with alizarin, amino- and nitroalizarins.

Divalent zinc, manganese, cobalt, nickel and trivalent yttrium form coloured compounds with 1,2-dihydroxy, 3-nitroanthraquinone (nitroalizarin), which do not find mention in the existing chemical literature. The results of spectrophotometric studies, elemental analysis, IR, TGA and molar conductance measurements on these complexes are presented in this paper.

3-Nitroalizarin (ICI, UK), recrystallized from chloroform, and reagent grade metal chlorides were used. $5 \times 10^{-4} M$ solution of the dye in ethanol was prepared by weighing. The ethanolic solutions of metal salts were prepared by dissolving the requisite amounts and standardized gravimetrically. Optical density measurements were made on a Bausch &

Lomb Spectronic-20 colorimeter. The ethanolic solutions of the metal chlorides were found to be almost neutral.

The wavelength of maximum absorption[4] was found to be 505, 505, 495, 505 and 500 nm for Zn, Mn, Co, Ni and Y complexes respectively. Job's[5] and molar ratio[6] methods in the concentration range of 4·5 to $10·0 \times 10^{-5}M$ in ethanolic medium were employed for finding out the composition of the complexes.

The ethanolic solutions of the metal salts and the dye in the molar ratio of 1:1 with slight excess of the dye were refluxed for several days until a solid residue was deposited. It was washed with a little chloroform and then with ethanol several times and dried *in vacuo*.

The IR spectra of the complexes were recorded on a Perkin-Elmer infracord model 137B in the range of 4000 to 600 cm^{-1} in KBr discs.

The thermograms of zinc, manganese, cobalt and nickel complexes were recorded between room temperature and 500° with a heating rate of 6°C/min. The per cent loss was plotted against the temperature.

Standard $2 \times 10^{-4}M$ solutions of the metal salts and the complexes were prepared in dimethyl sulphoxide and their molar conductances determined with a Philips conductivity bridge model PR 9500 using a dip-type conductivity cell.

The elemental analyses (Table 1) of the solid complexes confirm the ratio (1:1) ascertained from spectrophotometric studies. The log of apparent formation constant from Job's curves and the free energy of formation from $\Delta F = -RT \ln K$ were found to be $4·8 \pm 0·2$, $4·3 \pm 0·2$, $5·2 \pm 0·2$, $5·1 \pm 0·3$ and $4·0 \pm 0·2$ and $2·9 \pm 0·2$, $3·0 \pm 0·1$, $2·8 \pm 0·2$, $2·5 \pm 0·1$ and $2·7 \pm 0·1$ kcal/mole for Zn, Mn, Co, Ni and Y complexes respectively.

TABLE 1 — ANALYTICAL AND CONDUCTIVITY DATA OF THE COMPLEXES

Found (%) (calc.)*			ΛM of $2 \times 10^{-4}M$ soln (mhos)
N	Cl	M	
	$C_{14}H_8NO_6ZnCl.3H_2O$		
3·27 (3·29)	8·10 (8·07)	14·86 (14·89)	5·75
	$C_{14}H_8NO_6MnCl.3H_2O$		
3·22 (3·26)	8·25 (8·27)	12·78 (12·82)	5·60
	$C_{14}H_8NO_6CoCl.3H_2O$		
3·21 (3·23)	8·19 (8·20)	13·63 (13·62)	7·15
	$C_{14}H_8NO_6NiCl.3H_2O$		
3·25 (3·24)	8·20 (8·20)	13·61 (13·62)	5·00
	$C_{14}H_8NO_6YCl.3H_2O$		
3·00 (3·03)	7·71 (7·69)	— —	—

*Satisfactory C, H analyses have been obtained for the compounds.

The two hydroxyl groups of the dye seem to ionize while forming a complex with yttrium whereas in the case of zinc, manganese, cobalt and nickel, the ionization of C_1-OH group occurs and the C_2-OH group remains intact. Three water molecules also coordinate making these cations hexa-coordinate in these complexes.

The IR band assignments are based on the interpretation of Kiel and Heertjes[2]. The C_1-OH stretching frequency which occurs at 3030 cm^{-1} in the dye disappears in the complexes of Zn, Mn, Co and Ni whereas the C_2-OH stretching modes which occur at 3390 and 3226 cm^{-1} in the ligand still appear at 3390, 3226; 3390, 3333; 3390, 3279; and 3390 cm^{-1} in these complexes respectively. A hump at 3311 cm^{-1} in the yttrium complex may be assigned to OH stretch. C_9-CO stretch vibration which appears as a strong band at 1639 cm^{-1} in nitroalizarin becomes weak or is displaced to lower frequency in zinc, manganese, cobalt and nickel complexes but in yttrium complex it is split into two equally strong bands. The strong OH deformation mode at 1212 cm^{-1} in nitroalizarin is displaced to lower frequency in the complexes and the medium band at 1031 cm^{-1} in the ligand becomes very weak during complex formation. These facts indicate that the chelation with the ligand occurs at the oxygen of the C_1-OH group which ionizes and becomes a negative centre, and the oxygen of the C_9-CO group in the divalent metals.

TGA analyses of the complexes indicate that in the zinc complex the loss of three water molecules occurs between 80 and 190° resulting in the weight loss of 13·5% (12·30% theor.). Similarly, the weight losses are 13·0% (12·60% theor.) at 310°, 12·5% (12·48% theor.) at 210° and 12·0% (12·49% theor.) at 140 to 210° in Mn, Co and Ni complexes respectively. Since the water molecules are not easily eliminated and require higher temperatures for their removal, these must be tenaciously bound to the central metal atom and must be coordinated water and not lattice water.

The molar conductance values around 5·00-7·15 ohm^{-1} cm^2 indicate non-electrolytic nature of the complexes. Further, the complexes are completely water insoluble and hence they must be hexa-coordinate non-electrolytes of the general formulae, $[C_{14}H_8NO_6.MCl.3H_2O]$, where M = Zn, Mn, Co and Ni; and $[C_{14}H_5NO_6.YCl.3H_2O]$. These conclusions are further strengthened by the conductance value of 2·2 ohm^{-1} cm^2 $mole^{-1}$ reported for the non-electrolyte complex $[RuCl_3en]_2$ at a concentration of $10^{-3}M$ by Broomhead and Kane-Maguire[7].

Thanks are due to Prof. W. Rahman and the UGC, New Delhi, for help.

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Chapter Three

TRIPHENYLPHOSPHINE COMPLEXES OF TRANSITION METALS

13. COMPLEXES OF RUTHENIUM, OSMIUM, RHODIUM, AND IRIDIUM CONTAINING HYDRIDE CARBONYL, OR NITROSYL LIGANDS

Submitted by N. AHMAD,* J. J. LEVISON,* S. D. ROBINSON,* and M. F. UTTLEY*
Checked by E. R. WONCHOBA† and G. W. PARSHALL†

The increasing utility of triphenylphosphine derivatives of the platinum-group metals as homogeneous catalysts and as starting materials in preparative chemistry highlights the desirability of convenient small-scale syntheses for these compounds. Synthetic procedures in current use are frequently based on early methods involving heterogeneous reaction conditions and requiring use of multistage syntheses, prolonged reaction times, or dangerous reagents. The procedures described below are developed from a technique of synthesis devised by the present authors,[1,2] and permit the rapid synthesis of a wide range of triphenylphosphine derivatives of the platinum-group metals under homogeneous reaction conditions. The essentially homogeneous nature of each reaction solution,

*Department of Chemistry, King's College, Strand, London, WC2R 2LS, England. Present addresses: Department of Chemistry, Aligarh Muslim University, Aligarh, U.P. India (N.A.): International Nickel Limited, Bashley Road, London, N W. 10, England (J.J.L.).

†Central Research Department, E. I. du Pont de Nemours & Company, Wilmington, Del. 19898.

which is maintained until precipitation or crystallization of the required product occurs, renders these syntheses rapid, efficient, and highly selective. Thus variations of the basic technique involving changes in reaction temperature and solvent, concentration of ligands, and nature of added reagents provide routes to a range of pure triphenylphosphine derivatives. Moreover, the low solubility of most triphenylphosphine complexes in the alcoholic solvents employed in these reactions ensures the rapid precipitation or crystallization of the required product in good yield. The speed and selectivity are illustrated by the experimental details and the range of syntheses given. The efficiency is revealed in the high yields and good analytical data, the latter frequently obtained without recourse to purification procedures. Because of solubility considerations, these techniques are specific to the preparation of triphenylphosphine complexes.

A discussion of the basic technique, apparatus, and reagents employed together with details concerning methods of purification and characterization of products is given in the following section. The success of these syntheses is dependent on strict adherence to the procedures described.

General Technique

Platinum-group metal salts, $RuCl_3 \cdot 3H_2O$ (39% Ru),* $Na_2OsCl_6 \cdot 6H_2O$ (34% Os),† $RhCl_3 \cdot 3H_2O$ (39% Rh), and $Na_2IrCl_6 \cdot 6H_2O$ (34% Ir) are supplied by Johnson Matthey Limited and Engelhard Industries. Sodium tetrahydroborate or alcoholic potassium hydroxide, 40% w/v aqueous formaldehyde solution, and *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide serve as sources of hydride, carbonyl,[3] and nitrosyl ligands, respectively. The alcoholic reaction media are ethanol and 2-methoxyethanol, which are used without further purification. All reactions are performed in a 250-ml. conical (Erlenmeyer) reaction flask bearing an adapter fitted with a 30-cm. con-

*Commercial hydrated ruthenium trichloride has roughly this composition but contains a considerable number of distinct chemical species

†The readily available $(NH_4)_2OsCl_6$ is easily converted to the more soluble sodium salt by passage through a sodium-loaded sulfonic-acid-type ion-exchange resin (such as Rexyn 101) in hot aqueous solution

denser, a nitrogen inlet, and a stoppered port for the rapid introduction of reagent solutions. The flask is situated on a hot plate equipped with a magnetic stirrer to provide efficient heating and stirring of the reaction solutions.

The basic technique employed is common to all the syntheses described in this chapter and involves the *rapid, successive* addition of alcoholic solutions of the appropriate platinum-metal salt and other reagents to a vigorously stirred, boiling, alcoholic solution of triphenylphosphine, which is subsequently heated under reflux until precipitation of the required product commences or until the reaction is complete. In the latter instances the required products crystallize cleanly from the reaction solution on cooling. The success of these syntheses is critically dependent upon the maintenance of essentially homogeneous reaction conditions until the reaction sequence is complete. This in turn requires the addition of freshly prepared reagent solutions rapidly and successively in the specified order to the vigorously stirred, boiling reaction solution. Failure to observe this precaution leads to precipitation of insoluble intermediates, which may fail to react further and hence contaminate the reaction product.

The products are generally washed successively with ethanol (2 × 10 ml.), water (2 × 10 ml.), ethanol (2 × 10 ml.), and *n*-hexane (10 ml.) and dried *in vacuo*. Where necessary, further purification of products is achieved by recrystallization using solvents recommended in the literature (refer to individual syntheses for details). Products are characterized by analytical, spectroscopic, and melting-point data. The reported infrared spectra were recorded as Nujol mulls on a Perkin-Elmer 457-grating spectrometer. N.m.r. spectra were recorded on a Varian HA100 spectrometer with tetramethylsilane used as an internal standard. Although the complexes are all apparently air-stable in the crystalline state, all show appreciable *lowering* of melting point when recrystallized repeatedly from organic solvents in the presence of air. Recorded melting points correspond to the highest observed for a particular complex, and all are accompanied by decomposition. All complexes discussed are insoluble in alcohol, ether, or saturated hydrocarbon solvents; solubilities in benzene, chloroform, and dichloromethane are listed for specific complexes

A. CARBONYLCHLOROHYDRIDOTRIS(TRIPHENYLPHOSPHINE) RUTHENIUM(II)

$$RuCl_3 + 3(C_6H_5)_3P \xrightarrow{HCHO} RuHCl(CO)[P(C_6H_5)_3]_3$$

Carbonylchlorohydridotris(triphenylphosphine)ruthenium(II) was originally prepared by prolonged reaction of ruthenium trichloride and triphenylphosphine in basic alcoholic media.[4,5] It is more conveniently obtained from the homogeneous reaction of triphenylphosphine, ruthenium trichloride, and aqueous formaldehyde in boiling 2-methoxyethanol.[1]

Procedure

Solutions of 0.26 g. (1.0 mmole) of hydrated ruthenium trichloride in 20 ml. of 2-methoxyethanol and aqueous formaldehyde (20 ml., 40% w/v solution) are added rapidly and successively to a vigorously stirred, boiling solution of 1.58 g. (6 mmoles) of triphenylphosphine in 60 ml. of 2-methoxyethanol. The mixture is heated under reflux for 10 minutes and allowed to cool. The precipitate which forms is separated and washed successively with ethanol, water, ethanol, and *n*-hexane and dried *in vacuo*. Yield: 0.89 g. (93% based on $RuCl_3 \cdot 3H_2O$). *Anal.* Calcd. for $C_{55}H_{46}ClOP_3Ru$: C, 69.36; H, 4.87; Cl, 3.72; P, 9.76. Found: C, 69.3; H, 4.94; Cl, 3.36; P, 9.72.

Properties

Carbonyldihydridotris(triphenylphosphine)ruthenium(II) forms cream-white microcrystals which melt at 209–210° in air and at 235–237° in a capillary sealed under nitrogen. The infrared spectrum shows bands at 2020 (m), 1922 (vs), and 1903 (sh) cm.$^{-1}$ attributed to ν(CO) and ν(RuH). The complex is very sparingly soluble in benzene and slightly soluble in chloroform.

B. CARBONYLDIHYDRIDOTRIS(TRIPHENYLPHOSPHINE)-RUTHENIUM(II) (WHITE ISOMER)

$$RuCl_3 + 3(C_6H_5)_3P \xrightarrow[KOH]{HCHO} RuH_2(CO)[P(C_6H_5)_3]_3$$

Carbonyldihydridotris(triphenylphosphine)ruthenium(II) was originally prepared by boiling $RuCl_2[P(C_6H_5)_3]_3$ with sodium

borohydrate in benzene-ethanol or benzene-methanol (3:5) under hydrogen for one hour, then cooling the solution in a stream of hydrogen when white platelets of the required product crystallize during 15 hours. The procedure described below is a convenient single-step synthesis.[1]

Procedure

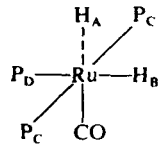
Solutions of 0.52 g. (2 mmoles) of hydrated ruthenium trichloride in 20 ml. of ethanol, aqueous formaldehyde (20 ml., 40% w/v solution), and 0.6 g. of potassium hydroxide in 20 ml. of ethanol are added quickly and successively to a boiling solution of 3.14 g. (12 mmoles) of triphenylphosphine in 140 ml. of ethanol. The solution is heated under reflux for 15 minutes and then cooled. The resultant gray precipitate is separated, washed successively with ethanol, water, ethanol, and *n*-hexane, and then dried *in vacuo*. Yield 1.3 g. (70% based on $RuCl_3 \cdot 3H_2O$).

The crude precipitate is dissolved in the minimum volume of warm benzene, and the solution is filtered and passed through a 9-in. × 1-in. column of activated neutral alumina. The benzene eluate is diluted with methanol, concentrated under vacuum at 25°, and then set aside to crystallize at 0°. Crystals of pure carbonyldihydridotris(triphenylphosphine)ruthenium(II) are filtered, washed with *n*-hexane, and dried *in vacuo*. *Anal.* Calcd. for $C_{55}H_{47}OP_3Ru$: C, 71.96; H, 5.16; P, 10.12. Found: C, 72.39, 71.8; H, 5.13, 5.2; P, 10.43, 9.7.

Recrystallization from dichloromethane-methanol affords a dichloromethane adduct, $RuH_2(CO)[P(C_6H_5)_3]_3 \cdot CH_2Cl_2$. *Anal.* Calcd. for $C_{56}H_{49}Cl_2OP_3Ru$: C, 67.0; H, 4.9; Cl, 7.05. Found: C, 67.0; H, 4.9; Cl, 6.9.

Properties

Carbonyldihydridotris(triphenylphosphine)ruthenium(II) forms white flaky microcrystals which melt at 160–162° in air and at 223–225° in a capillary sealed under nitrogen. The infrared spectrum shows bands at 1960 (m) and 1898 (m) cm.$^{-1}$, attributed to ν(RuH), and at 1940 (vs) cm.$^{-1}$, attributed to ν(CO). The high-field n.m.r. spectrum (benzene solution) comprises a complex first-order pattern of lines indicative of rigid stereochemistry (I)



I

H_A	τ16.47	$J(H_AP_D)$	15.5 Hz
		$H(H_AP_C)$	30.0 Hz
		$J(H_AH_B)$	6.0 Hz
H_B	τ18.33	$J(H_BP_D)$	73.5 Hz
		$J(H_BP_C)$	28.5 Hz
		$J(H_BH_A)$	6.0 Hz

The complex is moderately soluble in benzene, chloroform, and dichloromethane.

C. TRICARBONYLBIS(TRIPHENYLPHOSPHINE)-RUTHENIUM(0)

$$RuCl_3 + 2(C_6H_5)_3P \xrightarrow{KOH,\ HCHO} Ru(CO)_3[P(C_6H_5)_3]_2$$

Tricarbonylbis(triphenylphosphine)ruthenium(0) was first prepared by reducing $RuCl_2(CO)_2[P(C_6H_5)_3]_2$ with zinc dust in dimethylformamide at 100° under a carbon monoxide pressure of 4 atmospheres for 24 hours.[7] It has subsequently been prepared by treating $[Ru(CO)_3\{P(C_6H_5)_3\}]_3$ with excess triphenylphosphine in methyl ethyl ketone solution at 130–140° under an atmosphere of carbon monoxide,[8] and by an autoclave reaction of $Ru(CO)_5$ with triphenylphosphine in tetrahydrofuran at 130° under a nitrogen atmosphere.[9] Passage of carbon monoxide through a methanolic suspension of $RuH(OCOCH_3)[P(C_6H_5)_3]_3$ for *ca.* 12 hours also affords tricarbonylbis(triphenylphosphine)ruthenium(0).[10]

Procedure

Solutions of 0.39 g. (1.5 mmoles) of hydrated ruthenium trichloride in 30 ml. of cool 2-methoxyethanol, hot aqueous formaldehyde (30 ml., 40% w/v), and 0.6 g. of potassium hydroxide in 30 ml. of hot 2-methoxyethanol are added rapidly and successively to a well-stirred, boiling solution of 2.37 g. (9 mmoles) of triphenylphosphine in 90 ml. of 2-methoxyethanol. The reaction solution is stirred and heated under reflux for 1 hour and then cooled to room temperature. The resultant yellow microcrystalline precipitate is washed with ethanol, water, ethanol, and *n*-hexane and dried *in vacuo*. Yield 0.95 g (89% based on $RuCl_3 \cdot 3H_2O$). *Anal.* Calcd. for

$C_{54}H_{30}O_3P_2Ru$: C, 66.0; H, 4.26; P, 8.73. Found: C, 66.30, 66.0; H, 4.48, 4.2; P, 8.87.

Properties

Tricarbonylbis(triphenylphosphine)ruthenium(0) forms pale yellow microcrystals which melt at 170–173° in air and at 262–266° in a capillary sealed under nitrogen. The infrared spectrum shows a single very strong band at 1900 $cm.^{-1}$ attributable to $\nu(CO)$. The complex is moderately soluble in benzene and dichloromethane.

D. TRICHLORONITROSYLBIS(TRIPHENYLPHOSPHINE)-RUTHENIUM(II)

$$RuCl_3 + 2(C_6H_5)_3P + p\text{-}TolSO_2N(NO)(CH_3) \longrightarrow RuCl_3(NO)[P(C_6H_5)_3]_2$$

Trichloronitrosylbis(triphenylphosphine)ruthenium(II) was originally prepared by heating a mixture of $[RuCl_3(NO)]_n$ and triphenylphosphine in ethanol for 5–10 minutes.[11] It has subsequently been prepared by treating the complexes $RuCl(CO)(NO)[P(C_6H_5)_3]_2$[12] or $RuCl(NO)[P(C_6H_5)_3]_2$[13] with chlorine. The procedure described below is based on ruthenium trichloride and eliminates the need to use preformed ruthenium nitrosyl derivatives.

Procedure

Solutions of 0.39 g. (1.5 mmoles) of hydrated ruthenium trichloride in 30 ml. of ethanol and of 0.63 g. of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide in 30 ml. of ethanol are added in quick succession to a vigorously stirred, boiling solution of 2.37 g. (9 mmoles) of triphenylphosphine in 90 ml. of ethanol. The mixture is refluxed for 5 minutes and then cooled to room temperature. The green platelets deposited are filtered, washed with ethanol, water, ethanol, and *n*-hexane and are dried *in vacuo*. The green, impure complex is extracted with boiling dichloromethane (5 × 100 ml.). The extract is filtered, evaporated to small volume, and then allowed to crystallize at 0°. The crystals are washed with *n*-hexane. Yield is 0.92 g. (80% based on $RuCl_3 \cdot 3H_2O$). *Anal.* Calcd. for $C_{36}H_{30}Cl_3NOP_2Ru$:

C, 56.74; H, 3.97; Cl, 13.96; N, 1.84; P, 8.13. Found: C, 56.2; H, 3.98; Cl, 14.5; N, 1.81; P, 8.45.

Properties

Trichloronitrosylbis(triphenylphosphine)ruthenium(II) forms yellow-orange microcrystals which melt at 215–230° in air and at 290° in a capillary tube under nitrogen. The infrared spectrum shows a single band at 1873 (vs) cm.$^{-1}$ attributed to ν(NO). The impure green material shows a second infrared band at 1744 (w) cm.$^{-1}$. The complex is moderately soluble in benzene and dichloromethane.

E. DINITROSYLBIS(TRIPHENYLPHOSPHINE)RUTHENIUM

$$RuCl_3 + 2(C_6H_5)_3P + p\text{-}TolSO_2N(NO)CH_3) + (C_2H_5)_3N \longrightarrow Ru(NO)_2[P(C_6H_5)_3]_2$$

Dinitrosylbis(triphenylphosphine)ruthenium was first prepared by the present authors[1,14] using a synthesis similar to the one described below. It has subsequently been obtained by reacting preformed dihydridotris(triphenylphosphine)ruthenium(II) with nitric oxide,[15] and by reaction of $RuCl_2(CO)_2[P(C_6H_5)_3]_2$ with sodium nitrite in dimethylformamide.[16]

Procedure

A solution of 0.26 g. (1 mmole) of hydrated ruthenium trichloride in 20 ml. of ethanol is added to a stirred solution of 1.56 g. (6.0 mmoles) of triphenylphosphine in 60 ml. of boiling ethanol. Triethylamine (*ca.* 4 ml.) is then added dropwise until a deep-purple color develops. *N*-Methyl-*N*-nitroso-*p*-toluenesulfonamide (0.4 g.) in 20 ml. of ethanol and 6 ml. of triethylamine is added rapidly. The mixture is heated under reflux for 5 minutes, then allowed to cool. The gray precipitate is filtered, washed successively with ethanol, water, ethanol, and *n*-hexane and dried *in vacuo* to give the required complex. Yield is 0.55 g. (82% based on $RuCl_3 \cdot 3H_2O$). *Anal* Calcd. for $C_{36}H_{30}N_2O_2Ru$. C, 63.06; H, 4.41; N, 4.09; P, 9.03. Found C, 62.17; H, 4.13; N, 4.07; P, 8.26. The complex may be recrystallized from dichloromethane-methanol

Properties

Dinitrosylbis(triphenylphosphine)ruthenium forms orange-red microneedles which melt at 144–145° in air, and at 185–186° under nitrogen. The infrared spectrum shows bands at 1665 and 1619 cm.$^{-1}$. The complex is soluble in dichloromethane, chloroform, and benzene. $Ru(NO)_2[P(C_6H_5)_3]_2$ reacts with two molecules of oxygen to afford $Ru(O_2)(NO_3)(NO)[P(C_6H_5)_3]_2$.[16]

F. CARBONYLCHLOROHYDRIDOTRIS(TRIPHENYLPHOSPHINE)OSMIUM(II)

$$Na_2OsCl_6 \cdot 6H_2O + 3(C_6H_5)_3P \xrightarrow{HCHO} OsHCl(CO)[P(C_6H_5)_3]_3$$

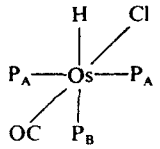
Carbonylchlorohydridotris(triphenylphosphine)osmium(II) was originally obtained by reacting ammonium hexachloroosmate(IV) and triphenylphosphine in a high-boiling alcoholic solvent[17] and subsequently correctly formulated as a hydridocarbonyl complex.[4,5,18] Optimum conditions reported for the synthesis involved a reaction time of 4.5 hours with temperature up to 190° and employed 2-(2-methoxyethoxy)ethanol–water mixture as solvent.[18]

Procedure

Solutions of 0.67 g. (1.2 mmoles) of sodium hexachloroosmate(IV) 6-hydrate in 35 ml. of 2-methoxyethanol and aqueous formaldehyde (15 ml., 40% w/v solution) are added in rapid succession to a vigorously stirred, boiling solution of 1.97 g. (7.5 mmoles) of triphenylphosphine in 75 ml. of 2-methoxyethanol. The reaction mixture is heated under reflux for 30 minutes, then allowed to cool to room temperature. During heating the color of the reaction mixture changes from brown-red to yellow. The off-white solid which precipitates is filtered, washed with ethanol, water, ethanol, and *n*-hexane, and dried *in vacuo*. Yield is 1.2 g. (95%). *Anal.* Calcd. for $C_{55}H_{46}ClOP_3Os$: C, 63.42; H, 4.45; P, 8.92. Found: C, 63.54; H, 4.7; P, 8.5.

Properties

Carbonylchlorohydridotris(triphenylphosphine)osmium(II) forms white microcrystals which melt with decomposition in air at 179–183° and at 289–290° in a capillary sealed under nitrogen. The infrared spectrum shows bands at 2099 (m) cm.$^{-1}$ attributed to ν(OsH) and at 1906 (vs) and 1891 (s) cm.$^{-1}$ attributed to ν(CO). The high-field n.m.r. pattern (benzene solution) comprises a doublet of triplets indicative of the stereochemistry II.



II

H	τ16.27	$J(HP_A)$	24.5 Hz
		$J(HP_B)$	87.0 Hz

The complex is moderately soluble in benzene, chloroform, and dichloromethane.

G. CARBONYLDIHYDRIDOTRIS(TRIPHENYLPHOSPHINE)-OSMIUM(II)

$$Na_2OsCl_6 \cdot 6H_2O + 3(C_6H_5)_3P \xrightarrow{KOH,\ HCHO} OsH_2(CO)[P(C_6H_5)_3]_3$$

Carbonyldihydridotris(triphenylphosphine)osmium(II) was first prepared by treating preformed $OsHCl(CO)[P(C_6H_5)_3]_3$ with sodium hydroxide in boiling 2-methoxyethanol.[19]

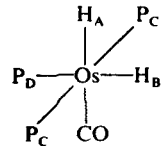
Procedure

Solutions of 0.84 g. (1.5 mmoles) of sodium hexachloroosmate(IV) 6-hydrate in 30 ml. of 2-methoxyethanol, aqueous formaldehyde (12 ml., 40% w/v solution), and 0.84 g. of potassium hydroxide in 15 ml. of 2-methoxyethanol are added rapidly and successively to a vigorously stirred, boiling solution of 4.72 g. (18 mmoles) of triphenylphosphine in 75 ml. of 2-methoxyethanol. The mixture is heated under reflux for 30 minutes, during which period the color changes to pale yellow and a white precipitate separates. The mixture is allowed to cool to room temperature. The off-white

precipitate is filtered, washed with ethanol, water, ethanol, and *n*-hexane, and dried *in vacuo*. Yield is 1.14 g. (73%). *Anal.* Calcd. for $C_{55}H_{47}OOsP_3$: C, 65.60; H, 4.70; P, 9.23. Found: C, 65.83; H, 4.64; P, 8.46.

Properties

Carbonyldihydridotris(triphenylphosphine)osmium(II) forms white microcrystals which melt at 202–204° in air and at 245–246° in a capillary sealed under nitrogen. The infrared spectrum shows bands at 2043 (m) and 1846 (m) cm.$^{-1}$ attributed to ν(OsH), and at 1947 (s) cm.$^{-1}$, attributable to ν(CO). The high-field n.m.r. pattern (benzene solution) comprises a complex order pattern of 24 lines.



III

H_A	τ17.34	$J(H_AP_D)$	16.5 Hz
		$J(H_AP_C)$	28.5 Hz
		$J(H_AH_B)$	4.7 Hz
H_B	τ18.91	$J(H_BP_D)$	69.5 Hz
		$J(H_BP_C)$	28.5 Hz
		$J(H_BH_A)$	4.7 Hz

The complex is moderately soluble in benzene, chloroform, and dichloromethane.

H. DICARBONYLDIHYDRIDOBIS(TRIPHENYLPHOSPHINE)-OSMIUM(II)

$$Na_2OsCl_6 \cdot 6H_2O + 2(C_6H_5)_3P \xrightarrow{KOH,\ HCHO} OsH_2(CO)_2[P(C_6H_5)_3]_2$$

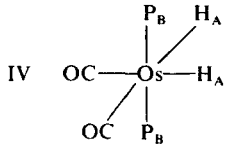
Dicarbonyldihydridobis(triphenylphosphine)osmium(II) was first prepared by allowing $OsH_2(CO)_4$ to react with three equivalents of triphenylphosphine in tetrahydrofuran at reflux temperature for 12 hours.[9] It has also been prepared by treatment of $Os(CO)_3[P(C_6H_5)_3]_2$ with hydrogen at 120 atmospheres pressure and 130° in tetrahydrofuran for 12 hours.[9] The yield was 50%, and the product was purified by fractional crystallization from *n*-heptane-tetrahydrofuran. The procedure described below[2] is a rapid, single-stage synthesis.

Procedure

Solutions of 1.18 g. (2.0 mmoles) of sodium hexachloroosmate(IV) 6-hydrate in 30 ml. of 2-methoxyethanol, aqueous formaldehyde (55 ml., 40% w/v solution), and 2.0 g. of potassium hydroxide in 20 ml. of 2-methoxyethanol are added rapidly and successively to a vigorously stirred, boiling solution of 0.92 g. (3.5 mmoles) of triphenylphosphine in 100 ml of 2-methoxyethanol. The very dark reaction mixture is heated under reflux for 30 minutes and slowly lightens in color. It is then allowed to cool to room temperature. The precipitated product is filtered, washed successively with ethanol, water, ethanol, and *n*-hexane, and dried *in vacuo*. Yield is 0.93 g. (57%). *Anal.* Calcd. for $C_{38}H_{32}O_2OsP_2$: C, 59.06; H, 4.17; P, 8.02. Found: C, 59.16; H, 4.48; P, 8.25.

Properties

Dicarbonyldihydridobis(triphenylphosphine)osmium(II) forms creamy-white microcrystals which melt at 243–244° in air and at 257–258° in a capillary sealed under nitrogen The infrared spectrum shows bands at 1926 (m) and 1871 (s) cm.$^{-1}$, attributed to ν(OsH), and 2020 (s) and 1990 (vs) cm.$^{-1}$, attributed to ν(CO). The high-field n.m.r. pattern (benzene solution) comprises a triplet indicative of stereochemistry IV.



H_A τ17 08 $J(H_AP_B)$ 22 75 Hz

The complex is moderately soluble in benzene, chloroform, dichloromethane, and tetrahydrofuran

I. TETRAHYDRIDOTRIS(TRIPHENYLPHOSPHINE) OSMIUM(IV)

$$Na_2OsCl_6 \cdot 6H_2O + 3(C_6H_5)_3P \xrightarrow{NaBH_4} OsH_4[P(C_6H_5)_3]_3$$

Tetrahydridotris(triphenylphosphine)osmium(IV) has been prepared by reaction of sodium hexachloroosmate(IV) or ammonium hexabromoosmate(II) with triphenylphosphine and sodium tetrahydroborate in boiling ethanol.[1,20]

Procedure

Solutions of 0.57 g. (1.0 mmole) of sodium hexachloroosmate(IV) 6-hydrate in 20 ml. of ethanol (filtered cold extract), and 0.2 g. of sodium tetrahydroborate in 20 ml. of ethanol are added rapidly and successively to a vigorously stirred, boiling solution of 1.57 g. (6.0 mmoles) of triphenylphosphine in 80 ml. of ethanol. Vigorous frothing occurs. The pink reaction solution is heated under reflux for 15 minutes, during which period a white precipitate appears. The precipitated product is filtered, washed successively with ethanol, water, ethanol, and *n*-hexane, and dried *in vacuo*. Yield is 0.95 g. (95%). *Anal.* Calcd. for $C_{54}H_{49}OsP_3$: C, 66.11; H, 5.03; P, 9.47. Found: C, 65.86; H, 5.21; P, 9.18.

Properties

Tetrahydridotris(triphenylphosphine)osmium(IV) forms creamy-white microcrystals which melt at 172–175° in air and at 219–221° in a capillary sealed under nitrogen. The infrared spectrum shows bands at 2086 (w), 2025 (m), 1951 (m), and 1891 (s) cm.$^{-1}$ attributed to ν(OsH). The high-field n.m.r. spectrum (benzene solution) comprises a 1:3:3:1 quartet [τ17.85, J(HP) 9 Hz.] which has been interpreted in terms of a nonrigid structure. The complex is sparingly soluble in benzene and dichloromethane.

J. TRICHLORONITROSYLBIS(TRIPHENYLPHOSPHINE)-OSMIUM(II)

$$Na_2OsCl_6 \cdot 6H_2O + 2(C_6H_5)_3P + p\text{-}TolSO_2N(NO)(CH_3) \longrightarrow OsCl_3(NO)[P(C_6H_5)_3]_2$$

Trichloronitrosylbis(triphenylphosphine)osmium(II) has been made by a multistage synthesis[21] and also by reaction of sodium hexachloroosmate, nitric oxide, and triphenylphosphine.[22] The procedure[1] eliminates use of gaseous nitric oxide

Procedure

Solutions of 1.12 g. (2.0 mmoles) of sodium hexachloroosmate(IV) 6-hydrate in 40 ml. of 2-methoxyethanol and 0.84 g. of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide in 40 ml. of 2-methoxyethanol are added rapidly and successively to a vigorously stirred, boiling solution of 3.16 g. (12 mmoles) of triphenylphosphine in 80 ml. of 2-methoxyethanol. The initially green solution is heated under reflux for 10 minutes and cooled to room temperature. The brown product precipitates and is filtered, washed with ethanol, water, ethanol, and *n*-hexane, and dried *in vacuo*. Yield is 1.12 g. (66%). *Anal.* Calcd. for $C_{36}H_{30}Cl_3NOOsP_2$: C, 50.80; H, 3.55; N, 1.65; P, 7.28; Cl, 12.5. Found: C, 51.11; H, 3.83; N, 1.49; P, 7.12; Cl, 13.1.

Properties

Trichloronitrosylbis(triphenylphosphine)osmium(II) forms brown microcrystals which melt at 265–290° in air and at 330° in a capillary sealed under nitrogen. The infrared spectrum shows a distinctive band at 1850 (vs) cm.$^{-1}$ attributed to ν(NO). The complex is slightly soluble in benzene and dichloromethane.

K. HYDRIDOTETRAKIS(TRIPHENYLPHOSPHINE)-RHODIUM(I)

$$RhCl_3 \cdot 3H_2O + 3(C_6H_5)_3P \xrightarrow{KOH} RhH[P(C_6H_5)_3]_4$$

Hydridotetrakis(triphenylphosphine)rhodium(I) has previously been prepared by addition of triphenylphosphine to preformed hydridotris(triphenylphosphine)rhodium(I) in toluene solution[23,24] and by reaction of preformed chlorotris(triphenylphosphine)-rhodium(I) with hydrazine and hydrogen in an ethanol-benzene medium containing excess triphenylphosphine.[23] Other syntheses employ aluminum alkyls,[25] Grignard reagents,[26] sodium propoxide,[27] and hydrogen under pressure[28] as reductants.

The procedure[1,2] given below affords an efficient, one-step synthesis of hydridotetrakis(triphenylphosphine)rhodium(I) from hydrated rhodium trichloride

Procedure

Hot solutions of 0.26 g. (1.0 mmole) of rhodium trichloride 3-hydrate in 20 ml. of ethanol and 0.4 g. of potassium hydroxide in 20 ml. of ethanol are added rapidly and successively to a vigorously stirred, boiling solution of 2.62 g. (10 mmoles) of triphenylphosphine in 80 ml. of ethanol. The mixture is heated under reflux for 10 minutes and allowed to cool to 30°. The precipitated product is filtered, washed with ethanol, water, ethanol, and *n*-hexane, and dried *in vacuo*. Yield 1.10 g. (97% based on $RhCl_3 \cdot 3H_2O$). *Anal.* Calcd. for $C_{72}H_{61}P_4Rh$: C, 75.0; H, 5.33; P, 10.73. Found: C, 74.69; H, 5.31; P, 10.52.

Properties

Hydridotetrakis(triphenylphosphine)rhodium(I) forms yellow microcrystals which melt at 145–147° in air and at 154–156° in a capillary sealed under nitrogen. The infrared spectrum shows a band at 2156 (m) cm.$^{-1}$ attributable to ν(RhH). The complex is soluble in benzene, chloroform, and dichloromethane.

L. CARBONYLHYDRIDOTRIS(TRIPHENYLPHOSPHINE)-RHODIUM(I)

$$RhCl_3 \cdot 3H_2O + 3(C_6H_5)_3P \xrightarrow{KOH,\ HCHO} RhH(CO)[P(C_6H_5)_3]_3$$

Carbonylhydridotris(triphenylphosphine)rhodium(I) was first prepared from $RhCl(CO)[P(C_6H_5)_3]_2$ by reduction with hydrazine in ethanolic suspension.[29] More recent syntheses involve reaction of $RhCl(CO)[P(C_6H_5)_3]_2$ with sodium tetrahydroborate[30] or triethylamine and hydrogen in ethanol[30] containing excess triphenylphosphine. Addition of ethanolic rhodium trichloride solution, aqueous formaldehyde, and ethanolic sodium tetrahydroborate to a boiling solution of triphenylphosphine in ethanol has also been employed to synthesize $RhH(CO)[P(C_6H_5)_3]_3$.[31] The following single-stage procedure[2] utilizes ethanolic potassium hydroxide in place of sodium tetrahydroborate.

Procedure

A solution of 0.26 g. (1.0 mmole) rhodium trichloride 3-hydrate in 20 ml. of ethanol is added to a vigorously stirred, boiling solution of 2.64 g. (10 mmoles) of triphenylphosphine in 100 ml. of ethanol. After a delay of 15 seconds, aqueous formaldehyde (10 ml., 40% w/v solution) and a solution of 0.8 g. of potassium hydroxide in 20 ml. of hot ethanol are added rapidly and successively to the vigorously stirred, boiling reaction mixture. The mixture is heated under reflux for 10 minutes and then allowed to cool to room temperature. The bright yellow, crystalline product is filtered, washed with ethanol, water, ethanol, and *n*-hexane, and dried *in vacuo*. Yield is 0.85 g. (94% based on $RhCl_3 \cdot 3H_2O$). *Anal.* Calcd. for $C_{55}H_{46}OP_3Rh$: C, 71.90; H, 5.05; P, 10.11. Found: C, 72.11; H, 5.17; P, 9.86.

Properties

Carbonylhydridotris(triphenylphosphine)rhodium(I) forms yellow microcrystals which melt at 120–122° in air and at 172–174° in a capillary tube under nitrogen. The infrared spectrum shows bands at 2041 (s) $cm.^{-1}$, attributed to ν(RhH), and at 1918 (vs), attributed to ν(CO). The high-field n.m.r. spectrum comprises a single signal at τ19.30, broadened by ligand dissociation and exchange processes. The complex is soluble in benzene, chloroform, and dichloromethane.

M. DICHLORONITROSYLBIS(TRIPHENYLPHOSPHINE)-RHODIUM(I)

$$RhCl_3 \cdot 3H_2O + 2(C_6H_5)_3P + p\text{-}TolSO_2N(NO)(CH_3) \longrightarrow RhCl_2(NO)[P(C_6H_5)_3]_2$$

Dichloronitrosylbis(triphenylphosphine)rhodium(I) was first prepared from $[RhCl(NO)_2]_x$ and triphenylphosphine.[32] It has subsequently been isolated by reacting chlorotris(triphenylphosphine)-rhodium(I) with nitric oxide in chloroform solution[33] and by adding triphenylphosphine to an ethanolic solution of "$RhCl_3$-(NO)"[34]

The following efficient single-stage procedure[1] avoids the use of nitric oxide

Procedure

Solutions of 0.39 g. (1.5 mmoles) of rhodium trichloride 3-hydrate in 30 ml. of ethanol and of 0.63 g. of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide in 30 ml. of ethanol are added rapidly and successively to a vigorously stirred, boiling solution of 3.93 g. (15 mmoles) of triphenylphosphine in 120 ml. of ethanol. The mixture is heated under reflux for 10 minutes and then cooled to room temperature. The precipitated brown product is filtered, washed with ethanol, water, ethanol, and *n*-hexane, and dried *in vacuo*. Yield is 1.08 g. (100% based on $RhCl_3 \cdot 3H_2O$). *Anal.* Calcd. for $C_{36}H_{30}Cl_2NOP_2Rh$: C, 59.36; H, 4.15; N, 1.92; Cl, 9.73; P, 8.50. Found: C, 59.70; H, 4.19; N, 1.79; Cl, 9.92; P, 8.82.

Properties

Dichloronitrosylbis(triphenylphosphine)rhodium(I) forms light-brown microcrystals which melt at 223–226° in air and at 278–279° in a capillary tube sealed under nitrogen. The infrared spectrum shows a band at 1630 (vs) $cm.^{-1}$ attributed to ν(NO). The complex is slightly soluble in benzene, chloroform, and dichloromethane.

N. NITROSYLTRIS(TRIPHENYLPHOSPHINE)RHODIUM

$$RhCl_3 \cdot 3H_2O + 3(C_6H_5)_3P + p\text{-}TolSO_2N(NO)(CH_3) \xrightarrow{KOH} Rh(NO)[P(C_6H_5)_3]_3$$

Nitrosyltris(triphenylphosphine)rhodium has previously been prepared by sodium-amalgam reduction of a mixture of rhodium nitrosyl chloride and triphenylphosphine in tetrahydrofuran.[32] Preparations from hydridotetrakis(triphenylphosphine)rhodium(I) and nitric oxide,[24] and from rhodium trichloride, nitric oxide, triphenylphosphine, and zinc dust have also been reported.[35] The following synthesis[1] is convenient and rapid

Procedure

Solutions of 0.26 g. (1.0 mmole) of rhodium trichloride 3-hydrate in 20 ml. of ethanol of 0.4 g. of *N*-methyl-*N*-nitroso-*p*-toluene-

sulfonamide in 20 ml. of ethanol and 0.4 g. of potassium hydroxide in 20 ml. of ethanol are added in rapid succession to a well-stirred solution of 2.62 g. (10.0 mmoles) of triphenylphosphine in 80 ml. of boiling ethanol. This mixture is heated under reflux for 10 minutes, cooled to 30°, and then filtered. The red precipitate is washed successively with ethanol., water, ethanol, and *n*-hexane, and dried *in vacuo*. Yield is 0.8 g. (87% based on $RhCl_3 \cdot 3H_2O$). *Anal.* Calcd. for $C_{54}H_{45}NOP_3Rh$: C, 70.52; H, 4.93; N, 1.52; P, 10.1. Found: C, 70.44; H, 4.76; N, 1.4; P, 9.84.

Properties

Nitrosyltris(triphenylphosphine)rhodium forms bright crimson-red microcrystals. It softens at 96°, then melts with decomposition at 160° in air; sealed under nitrogen it melts at 205–206°. The infrared spectrum shows a peak at 1610 cm.$^{-1}$ (vs) attributed to ν(NO). The complex is soluble in dichloromethane, chloroform, and benzene.

O. DICHLORONITROSYLBIS(TRIPHENYLPHOSPHINE)-IRIDIUM(I)

$$Na_2IrCl_6 \cdot 6H_2O + 3(C_6H_5)_3 + p\text{-}TolSO_2(NO)(CH_3) \longrightarrow IrCl_2(NO)[P(C_6H_5)_3]_2$$

Dichloronitrosylbis(triphenylphosphine)iridium(I) was first prepared by treating $[Ir(NO)_2\{P(C_6H_5)_3\}_2]ClO_4$ with hydrogen chloride[37] and has subsequently been obtained by a similar reaction involving $Ir(NO)[P(C_6H_5)_3]_3$.[38] Reactions of triphenylphosphine with preformed $IrCl_2(NO)(C_8H_{12})$ in boiling acetone, or with hydrated iridium trichloride and nitric oxide in boiling methanol also afford dichloronitrosylbis(triphenylphosphine)iridium(I).[33] The following procedure[1] is quick and efficient and eliminates the use of nitric oxide.

Procedure

Solutions of 1.40 g. (2.5 mmoles) of sodium hexachloroiridate(IV) 6-hydrate in 50 ml. of 2-methoxyethanol and of 1.05 g. of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide in 50 ml. of the same solvent are

added rapidly and successively to a vigorously stirred, boiling solution of 3.95 g. (15 mmoles) of triphenylphosphine in 100 ml. of 2-methoxyethanol. The mixture is stirred and heated under reflux for 5 minutes, then allowed to cool to room temperature. The precipitated product is filtered, washed with ethanol, water, ethanol, and *n*-hexane, and dried *in vacuo*. Yield is 1.05 g. (52%). *Anal.* Calcd. for $C_{36}H_{30}Cl_2NOP_2Ir$: C, 52.88; H, 3.70; Cl, 8.67; N, 1.71; P, 7.58. Found: C, 53.4; H, 3.73; Cl, 8.46; N, 1.64; P, 7.60.

Properties

Dichloronitrosylbis(triphenylphosphine)iridium(I) forms orange-yellow microcrystals which melt at 247–252° in air and at 308–309° in a capillary tube sealed under nitrogen. The infrared spectrum shows a band at 1560 (vs) cm.$^{-1}$ attributed to ν(NO). The complex is moderately soluble in benzene, chloroform, and dichloromethane.

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14. FLUORO COMPLEXES OF RHODIUM(I) AND IRIDIUM(I)

Submitted by L. VASKA* and J. PEONE, JR.*,†
Checked by E. R. WONCHOBA‡ and G. W. PARSHALL‡

The compounds described here, *trans*-$[MF(CO)(Ph_3P)_2]$, in which M = Ir or Rh,[1-3] are useful as starting materials for a one-step convenient preparation of a variety of compounds of these metals:[2]

$$trans\text{-}[MF(CO)(Ph_3P)_2] + M'A \longrightarrow trans[MA(CO)(Ph_3P)_2] + M'F$$

*Department of Chemistry, Clarkson College of Technology, Potsdam, N.Y 13676.
†Present address: Department of Chemistry, Broome Community College, Binghamton, N.Y. 13902.
‡Central Research Department, Experimental Station, E. I. du Pont de Nemours & Company, Wilmington, Del 19898

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Schiff Base Complexes of Ti(III)

S. FAKHRUL HASAN RIZVI & NASEER AHMAD
Department of Chemistry, Aligarh Muslim University
Aligarh

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Complexes of Ti(III) with eight Schiff bases have been prepared in tetrahydrofuran. The elemental analyses show them to have the general formula $TiCl_3$(Schiff base).XH_2O, where X varies from 0 to 2. Complexes show magnetic moments in the range 1·44-1·75 BM. The molar conductances of their $10^{-3}M$ solutions in DMSO are between 22·7 and 70·6 ohm^{-1} cm^2 $mole^{-1}$, showing thereby that the complexes are 1 : 1 electrolytes. Thermogravimetric analyses confirm the presence of water. Coordination of the ligands through nitrogen of C=N group is suggested by a shift in $\nu_{C=N}$ to higher frequency region in the complexes as compared to the ligands.

A LARGE number of metal complexes of Schiff bases have been reported in literature[1,2] including those with Ti(IV)[3,4]. However, no work has been done on the complexes of Ti(III) with Schiff bases. We report here the results of our studies on the complexes of Ti(III) with Schiff bases, bis-(vanillin)-benzidine, bis(vanillin)-dianisidine, bis-(vanillin)-*o*-phenylenediimine, bis(vanillin)-ethylenediimine, bis(vanillin)-propylenediimine, bis(salicylidene)*o*-phenylenediimine, bis(benzylidene)-ethylenediimine and bis(benzylidene)-*o*-phenylenediimine.

Benzidine (Reanal, Hungary), dianisidine (E. Merck) ethylenediamine (Riedel), *o*-phenylenediamine (Xenon, Poland), propylenediamine (Fluka), benzaldehyde (Norda, USA), salicylaldehyde (Riedel), vanillin (Bush Boake, Allen, London) and titanium (III) chloride (crystallized as $TiCl_3.6H_2O$)[5] were used for the preparation of the complexes.

The respective aldehydes and amines were taken in the molar ratio of 2:1 in benzene, stirred for 3-5 hr and the resulting precipitate washed with benzene and crystallized. The purity of the ligands was checked by elemental analysis.

The complexes were prepared by mixing $TiCl_3$ and the respective Schiff bases in 1:1 molar ratio, with a slight excess of the latter in dry tetrahydrofuran. The preparations were carried out in a dry inert atmosphere because Ti(III) is susceptible to oxidation from air and prone to hydrolysis from moisture.

Molar conductance was measured using conductivity bridge model PR 9500 having a dip-type conductivity cell. The magnetic moments of the solid specimens were determined by Gouy method. Diamagnetic correction for the ligands was applied.

TGA curves were taken, using a Bausch & Lomb thermogravimetric balance at a heating rate of 6°/min in the temperature range 30-520° under inert atmosphere.

The IR spectra of the complexes and the ligands (in KBr) were taken in the range 4000-200 cm^{-1} on a Perkin-Elmer infrared spectrophotometer model 621.

The complexes have a 1:1 (metal: ligand) stoichiometry (Table 1). The magnetic susceptibilities of the complexes lie in the range 1·39-1·82 BM showing that the metal is in the trivalent state. The values, lower than 1·73 BM might be due to a slight oxidation of the complex. A similar behaviour has been observed previously in the Ti(III)-*o*-phenanthroline complex[6].

The molar conductances of the complexes in DMSO lie between 22·7 and 70·5 ohm^{-1} cm^2 $mole^{-1}$. This range is quite compatible with the values reported

TABLE 1 — COLOUR, ANALYTICAL* AND MAGNETIC MOMENT DATA OF THE Ti(III) COMPLEXES

Complex	Nitrogen (%)	Chloride (%)	Colour
[Dichloro bis(vanillin)-benzidine]Ti(III) chloride $[C_{28}H_{24}N_2O_4Cl_2Ti]Cl$ ($\mu_{eff.}$ = 1·39 BM)	5·04 (4·91)	17·49 (17·78)	Reddish brown
[Dichloro bis(vanillin)-dianisidine]Ti(III) chloride $[C_{30}H_{28}N_2O_6Cl_2Ti]Cl$ ($\mu_{eff.}$ = 1·49 BM)	4·21 (4·30)	15·89 (15·72)	Dark brown
[Dichlorodiaquo bis(vanillin)-*o*-phenylenediimine]Ti(III) chloride $[C_{22}H_{20}N_2O_4.2H_2OCl_2Ti]Cl$	5·91 (5·95)	19·37 (19·08)	Yellow
[Dichlorodiaquo bis(vanillin)-ethylenediimine]Ti(III) chloride $[C_{18}H_{20}N_2O_4.2H_2OCl_2Ti]Cl$ ($\mu_{eff.}$ = 1·48 BM)	6·50 (6·43)	19·58 (19·49)	Yellow
[Dichloro bis(vanillin)-propylenediimine]Ti(III) chloride $[C_{19}H_{22}N_2O_4Cl_2Ti]Cl$ ($\mu_{eff.}$ = 1·59 BM)	5·60 (5·55)	22·60 (22·53)	Dark yellow
[Dichloro bis (salicylidene)-*o*-phenylenediimine]Ti(III) chloride $[C_{20}H_{16}N_2Cl_2Ti]Cl$	5·95 (5·90)	22·59 (22·73)	Dark brown
[Dichloro bis(benzylidene)-ethylenediimine]Ti(III) chloride $[C_{16}H_{16}N_2Cl_2Ti]Cl$	6·16 (5·99)	34·38 (34·23)	Light yellow
[Dichloro bis(benzylidene)-*o*-phenylenediimine]Ti(III) chloride $[C_{20}H_{16}N_2Cl_2Ti]Cl$ ($\mu_{eff.}$ = 1·82 BM)	6·38 (6·32)	24·24 (24·36)	Light yellow

*Satisfactory values for carbon and hydrogen were obtained

for 1:1 electrolytes[7,8]. This indicates that one of the three chlorine atoms is not coordinated to the metal ion.

Elemental analyses show the presence of two water molecules in bis(vanillin)-*o*-phenylenediimine and bis(vanillin)-ethylenediimine complexes. TGA curves show that the elimination of two water molecules is completed at 125° in bis(vanillin)-*o*-phenylenediimine complex (observed loss 6·5%, theoretical for two water molecules = 6·2%) and 190° in bis(vanillin)-ethylenediimine complex (observed loss = 6·2%, theoretical for 2 water molecules = 6·9%). The two water molecules thus seem to be coordinated, making the titanium atom hexacoordinated in these two cases whereas in the remaining six complexes, it is tetracoordinated.

The IR spectrum shows a hump in the range 3500-3400 cm^{-1} in the case of these two complexes, which is the region of antisymmetric OH stretching. Wagging or rocking mode of coordinated water[9] in many compounds has been observed between 880 and 650 cm^{-1}. Since the ligands also absorb in this region, it is not possible to assign any bands, in the spectra of their complexes, to vibrations of coordinated water with certainty.

A band appearing in the range 1625-1630 cm^{-1} in the spectra of ligands shifts to the region 1630-1650 cm^{-1} in the spectra of their complexes. This band may be due to $\nu_{C=N}$ and its shift to higher frequencies indicates coordination through the nitrogen of the C=N group[10].

There is very little change in the IR spectrum in the region of OH deformation (1200 and 1410-1310 cm^{-1}) indicating that the hydroxyl group is not taking part in coordination in the bis(salicylidene)-*o*-phenylenediimine complex.

The spectra of Ti(III) complexes are very complicated in the region 700-400 cm^{-1}. However, there are a few bands observed in the complexes which are absent in the ligands. These can be assigned to metal-chlorine and metal-nitrogen bonds. Thus, bands at 380, 350, 345, 430, 340 and 380 cm^{-1} have been tentatively assigned to ν_{M-N} and bands at 490, 540, 630, 540, 615 and 595 cm^{-1} to ν_{M-Cl}.

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STUDIES ON THE MIXED LIGAND COMPLEXES OF RARE EARTHS WITH DIPIVALOYLMETHANE AND PYRAZINE

M SHAMEEM ANSARI and NASEER AHMAD
Department of Chemistry, Aligrah Muslim University, Aligarh, U P , India

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Abstract—The mixed ligand complexes, tris(dipivaloylmethanato) pyrazinates of trivalent lanthanide (except Ce, Pm and Lu) and yttrium ions were synthesised and characterised by elemental analyses, melting points, thermogravimetric analyses, magnetic moments, molar conductances and ir spectrum The complexes are Ln(dpm)$_3$Pz where Ln = trivalent lanthanide or yttrium ion, dpm = dipivaloylmethane and Pz = pyrazine The melting points decrease with increase in atomic number The dipivaloylmethane is lost before pyrazine on heating under nitrogen The complexes are non-electrolytes The magnetic moments are normal The ir spectra are discussed

INTRODUCTION

NUMEROUS papers dealing with the use of rare-earth β-diketonates as pseudo-contact NMR shift reagents[1–6] have appeared Some of these β-diketonates have been used for the gas chromatographic[7, 8] separation of lanthanides various workers have prepared mixed ligand complexes of rare-earths with oxygen and nitrogen containing Lewis bases. Charles and Ohlmann[9] reported 1 1 and 1 2 adducts of tris-(dibenzoylmethane) europium(III) with a number of nitrogen and oxygen containing ligands Schwarberg *et al* [10] have reported Ln(dpm)$_3$DMF (dpm = dipivaloylmethane, Ln = lanthanide ion, DMF = dimethylformamide) adducts. A few adducts which contain one molecule of either 2,2'-dipyridyl or 1,10-phenanthroline attached to tris-β-diketonates of the lanthanide ions have also been described[11–13] Selbin, Ahmad and Bhacca[14] described rare-earth dipivaloylmethanates and their adducts with pyridine, 2,2'-dipyridyl and 1,10-phenanthroline.

The present communication deals with the synthesis of the Y and Ln(dpm)$_3$ (except Pm, Ce and Lu) adducts with pyrazine and their elemental analyses, m.p., thermograms, magnetic moments, molar conductance values and i.r. spectra.

EXPERIMENTAL

Rare-earth halides (Leico Chemicals, U S A) and YCl$_3$ (E Merck, Germany) were used to prepare the complexes 2,2,6,6-tetramethyl-3,5-heptanedione (dipivaloylmethane, Penn Chem Research, U S A) was used as such

Preparation of complexes Tris(dipivaloylmethane) lanthanide(III) compounds were synthesised by the method of Eisentraut and Sievers[7], and Berg and Acosta[8] A solution of the lanthanide chloride in 1 1 ethanol–water was mixed with an ethanolic solution of the sodium salt of dipivaloylmethane The chelate precipitated, was washed and recrystallised from *n*-hexane

The lanthanide complex obtained was mixed with pyrazine in the molar ratio of 1 1 in *n*-hexane and allowed to crystallize when mixed ligand complexes were obtained in all cases except cerium

Physico-chemical methods The compounds were subjected to elemental analyses for carbon, hydrogen and nitrogen The melting points were determined The molar conductances of 10^{-3}M solutions of the complexes in methanol were measured on a Philips PR 9500 conductivity bridge using a dip type cell The magnetic measurements were made at room temperature with a Gouy balance. Diamagnetic corrections for the ligand were applied and the values of effective magnetic moments calculated (Table 1) The ir spectra of the dipivaloylmethanates and the mixed ligand complexes were taken in KBr discs with a Perkin Elmer Infracord model 137B in the range 4000–600 cm^{-1}

RESULTS AND DISCUSSION

Elemental analyses show that the interaction of lanthanide (dpm)$_3$ and pyrazine gives a 1:1 adduct of the general formula, M(dpm)$_3$·Pz, where M stands for the trivalent yttrium and rare-earths except cerium, promethium and lutetium and Pz for pyrazine.

The mixed ligand complexes are quite stable and do not decompose before melting. They melt sharply between 165 and 218°C. The melting points fall as the atomic number of the lanthanide increases. The thermograms of praseodyium, europium, dysprosium, thulium and yttrium complexes present interesting features. The five thermograms are similar in shape with rapid weight loss at 245, 230, 205, 200 and 200°C in the respective complexes There is a gradual decrease in the temperature of maximum rate of weight loss with increase in atomic number of the rare-earth element. The thermogram shows that the loss of one dipivaloylmethane is slow, of the second rapid and the third again slow while the pyrazine seems to be lost only after the removal of dipivaloylmethane. In Pr(dpm)$_3$ Pz there is a weight loss of about 11% at 338°C (theoretical for one Pz molecule = 10·38%), a weight loss of about 24% up to 235°C and 68% up to 335°C (theoretical weight losses for one Pz and 3 dpm molecules are 23·7 and 71·1% respectively). The total weight loss is approx. 83% The same is the pattern of thermogravimetric curves with europium, dysprosium, thulium and yttrium with greater weight loss in the second stage and total weight loss of 93% (theoretical wt loss for 3 dpm and 1 Pz = 80·6%), 87% (theo. 79·5%), 90% (theo. 78·9%) and 84·5% (theo. 87·7%) respectively. It is, therefore, definite that with the loss of dipivaloylmethane and pyrazine there is sublimation of the chelate species at various stages.

The practically observed weight loss is therefore higher than the weight loss calculated for the removal of 3 dpm and one pyrazine molecules in the cases of europium, dysprosium and thulium. This, however, is not the case with yttrium.

The complexes can be recrystallized from *n*-hexane, chloroform or carbon tetrachloride and can be handled in moist air without reaction. The complexes are insoluble in water but soluble in almost all organic solvents indicating that they are complex non-electrolytes. Their molar

Table 1 Analysis and some characterizing data

	Compounds	Colour		%C	%H	%N	M p (°C)	M p Moment (B M)	Molar Cond ($\Omega^{-1}cm^2mole^{-1}$)
1	La(dpm)$_3$Pz	White	Calcd	57 76	7 92	3 64	218	Diamag	0 54
			Found	57 87	8 19	3 55			
2	Pr(dpm)$_3$Pz	Light green	Calcd	57 62	7 91	3 63	217–220	3 6	0 47
			Found	57 11	7 80	3 72			
3	Nd(dpm)$_3$Pz	Violet	Calcd	57 57	7 86	3 62	220	3 65	0 38
			Found	57 10	8 01	3 86			
4	Sm(dpm)$_3$Pz	White	Calcd	56 99	7 82	3 59	217	2 15	0 34
			Found	56 78	8 18	3 55			
5	Eu(dpm)$_3$Pz	White	Calcd	56 89	7 81	3 58	211–214	3 77	0 33
			Found	57 33	7 79	3 55			
6	Gd(dpm)$_3$Pz	White	Calcd	56 49	7 75	3 56	207–211	7 51	0 33
			Found	56 83	7 56	3 35			
7	Tb(dpm)$_3$Pz	White	Calcd	56 37	7 74	3 54	200–203	10 12	0 24
			Found	56 83	7 56	3 35			
8	Dy(dpm)$_3$Pz	White	Calcd	56 11	7 71	3 53	195–198	10 73	0 20
			Found	55 61	7 70	3 70			
9	Ho(dpm)$_3$Pz	Light yellow	Calcd	55 95	7 68	3 53	183–187	10 73	0 37
			Found	56 02	7 90	3 44			
10	Er(dpm)$_3$Pz	Pink	Calcd	55 79	7 66	3 52	168–171	7 56	0 21
			Found	55 72	7 60	3 38			
11	Tm(dpm)$_3$Pz	White	Calcd	55 70	7 63	3 51	168–171	7 56	0 21
			Found	54 75	7 78	3 61			
12	Yb(dpm)$_3$Pz	White	Calcd	55 33	7 1	3 48	165	4 67	0 15
			Found	55 75	7 16	3 71			
13	Y(dpm)$_3$Pz	White	Calcd	56 58	7 93	3 89	185	Diamag	0 35
			Found	56 88	7 73	3 97			

dpm = dipivaloylmethane, Pz = Pyrazine

conductances in methanol at 10^{-3} M concentration are in the range 0 15–0 54 $\Omega^{-1}cm^2mole^{-1}$ which proves they are non electrolytes since the molar conductance ranges for 10^{-3} M solutions in methanol are 80–115, 160–220 and 290–350 $\Omega^{-1}cm^2mole^{-1}$ for 1 1, 2 1 and 3 1 electrolytes respectively[15]

The magnetic susceptibilities of these complexes after applying diamagnetic correction for the ligand show the usual double humped curve when plotted against the atomic number of the rare-earth elements

The ir spectrum of neodymium tris-dipivaloyl-methanate contains bands at 1560 cm^{-1}(s) due to C=C, 1475 cm^{-1}(s) due to C=O and CH, 1361 cm^{-1}(s) and 1333 cm^{-1}(s) due to CH deformations, 1260 cm^{-1}(m) due to C–C and C–CH_3, 1168 cm^{-1}(m) due to C–H and 1114 cm^{-1}(s) due to $(CH_3)_2$–C skeletal vibrations These are tentative assignments taken from Bellamy[16] Similar bands occur in other dipivaloyl-methanates

The most important bands in pyrazine are at 3155 and 3059 cm^{-1} (hydrogen stretching), 1709 and 1522 cm^{-1} (interaction between C=C and C=N vibrations), 1408 cm^{-1} (ring vibrations), 1149, 1130, 1062 cm^{-1} (H-bending), 1020–1005 cm^{-1} (ring vibrations) and a very strong band at 787 cm^{-1} (H bending)[17] In KBr phase, pyrazine shows very strong bands at 3155, 1522, 1408, 1149, 1062, 1030, 1005 and 787 cm^{-1}

When pyrazine forms an adduct with the rare-earth dipivaloylmethanates, all the bands of pyrazine disappear except those at 1403(s), 1389(s), 1399(s), 1406(s), 1401(s), 1405(s) 1408(s) 1408(s) 1408(s) 1408(s) 1405(s) 1408(m) cm^{-1} in lanthanum, praseodymium, neodymium samarium, europium, gadolinium, terbium, dysprosium, holmium erbium, thulium and ytterbium tris dipivaloylmethanato pyrazinates These bands may be due to the interaction between C=C and C=N vibrations of the portion of the pyrazine molecule where nitrogen does not coordinate with the metal The bands at 1340(s) 1333(s) 1344(s), 1337(s), 1340(s), 1379(m), 1215(m), 1342(s) 1212(s) and 1172(m) cm^{-1} appear in the tris dipivaloylmethanates of lanthanum, neodymium europium, gadolinium terbium, dysprosium, holmium, erbium thulium and ytterbium but disappear in the corresponding tris dipivaloylmethanatopyrazinates

It is concluded that the rare-earth have a strong tendency to increase their coordination number from six to seven and to give heptacoordinate complexes of considerable stability

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VO(II), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Ru(III), Rh(III), Pd(II), Pt(IV) & Au(III) Complexes of Benzidine

S. M. F. RAHMAN, NASEER AHMAD & VIJAY KUMAR
Department of Chemistry, Aligarh Muslim University, Aligarh

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VO(II), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Ru(III), Rh(III), Pd(II), Pt(IV) & Au(III) Complexes of Benzidine

S. M. F. Rahman, Naseer Ahmad & Vijay Kumar

Department of Chemistry, Aligarh Muslim University
Aligarh

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Benzidine forms 1 : 1 complexes with VO(II) sulphate and chlorides of Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) and 2 : 1 complexes with chlorides of Ru(III), Rh(III), Pd(II), Pt(IV) and Au(III). The 1 : 1 complexes have tetracoordinate and 2 : 1 probably hexacoordinate geometry. The molar conductances of the complexes in dimethyl sulphoxide are similar to those of the parent salts. It is suggested that dimethyl sulphoxide enters the coordination sphere displacing the coordinated chlorides. The magnetic data support this suggestion. The nature of coordination is discussed in the light of IR spectral data.

THE complexes of benzidine with vanadyl sulphate and the chlorides of Fe(III), Ni(II), Zn(II), Cd(II), Hg(II), Ru(III), Rh(III), Pt(IV) and Au(III) find no mention in the existing literature. The complexes with the chlorides of Mn(II)[1,2], Co(II)[3], Cu(II)[4] and Pd(II)[5] are reported in literature but are not well characterized. The preparation of the above metal complexes and their characterization on the basis of magnetic, conductance and IR data are described in this note.

Benzidine (E. Merck), vanadyl sulphate and chlorides of Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Cd(II), Hg(II) (BDH, Analar), Zn(II) (Riedel), Ru(III), Rh(III), Pd(II), Pt(IV) (aq. HCl solution) and Au(III) (JM, UK) were used to prepare the complexes.

The ethanolic solutions of the metal salts and benzidine were mixed in 1 : 2 molar ratio with a slight excess of the amine, and the mixture warmed on a water-bath for a few minutes. The precipitates obtained were centrifuged, washed with a little ether, with ethanol several times and dried *in vacuo*

Table 1 — Colour, Analytical, Magnetic Moment and Conductance Data of the Complexes

Compound	Colour	Found (calc.)				Decomp. temp. (°C)	$\mu_{eff.}$ (BM)	Λ_M of $10^{-3}M$ solution (ohm^{-1} cm^2 mole^{-1})
		C(%)	H(%)	N(%)	Cl or SO_4(%)			
VO.L.SO_4	Greyish green	41·49 (41·52)	3·42 (3·46)	8·08 (8·07)	27·70 (27·71)	210	1·73	17·92
Mn.L.Cl_2	Cream	46·45 (46·48)	3·85 (3·87)	9·00 (9·03)	22·92 (22·89)	260	5·76	48·80 (45·92)*
Fe.L.Cl_3	Light brown	41·70 (41·72)	3·45 (3·45)	8·09 (8·11)	30·76 (30·79)	160	6·06	30·80
Co.L.Cl_2	Blue	45·78 (45·80)	3·85 (3·82)	8·89 (8·92)	22·60 (22·59)	293	4·27	48·16 (48·64)
Ni.L.Cl_2	Light green	45·90 (45·93)	3·84 (3·82)	8·90 (8·93)	22·61 (22·61)	160	D	49·28 (48·72)
Cu.L.Cl_2	Dark brown	45·20 (45·23)	3·74 (3·76)	8·76 (8·79)	22·30 (22·26)	220	1·92	33·60 (33·60)
Zn.L.Cl_2	White	44·97 (44·98)	3·72 (3·74)	8·76 (8·74)	22·00 (22·14)	255	D	6·72
Cd.L.Cl_2	White	39·22 (39·20)	3·24 (3·26)	7·60 (7·62)	19·31 (19·30)	250	D	11·20
Hg.L.Cl_2	Light yellow	31·62 (31·62)	2·64 (2·63)	6·15 (6·14)	15·53 (15·57)	210	D	3·36
Ru.L_3.Cl_3	Dark blue	49·99 (50·05)	4·15 (4·17)	9·71 (9·73)	18·46 (18·47)	230	1·95	23·52 (24·08)
Rh.L_2.Cl_3	Dirty brown	49·91 (49·89)	4·15 (4·15)	9·72 (9·70)	18·39 (18·41)	210	D	24·64 (22·98)
Pd.L_2.Cl_2	Brown	52·90 (52·82)	4·38 (4·40)	10·30 (10·27)	13·11 (13·00)	240	D	8·40
Pt.L_2.Cl_4	Steel grey	40·84 (40·86)	3·41 (3·40)	7·94 (7·94)	20·12 (20·11)	Above 360	D	47·60
Au.L_2.Cl_3	Dark blue	42·89 (42·90)	3·56 (3·57)	8·35 (8·34)	15·89 (15·83)	160	D	47·60 (49·28)

*Values in parentheses are molar conductances for the simple salts used for the synthesis of the complexes
L: ligand; D: diamagnetic.

at room temperature. The complexes were analysed for C, H, N and Cl or SO_4.

Standard solutions ($10^{-3}M$) of the complexes and of the corresponding simple metal salts were prepared in dimethyl sulphoxide and their molar conductances were measured on a Philips conductivity bridge, model PR 9500. Vanadyl sulphate and the chlorides of Fe, Zn, Cd, Hg and Pd did not dissolve in dimethyl sulphoxide and hence their molar conductances could not be measured.

The magnetic measurements were made at room temperature, with the help of a Gouy balance. Diamagnetic correction was also applied. The IR spectra were recorded in the range of 4000-600 cm^{-1} in nujol.

$VOSO_4$, $MnCl_2$, $FeCl_3$, $CoCl_2$, $NiCl_2$, $CuCl_2$, $ZnCl_2$ and $HgCl_2$ form 1:1 complexes with benzidine while $RuCl_3$, $RhCl_3$, $PdCl_2$, $PtCl_4$ and $AuCl_3$ form 1:2 complexes (Table 1).

νNH of the ligand at 3337 cm^{-1} does not register much shift in the spectra of the complexes. Two strong bands at 1635 and 1615 cm^{-1} in the ligand which are assigned to NH_2 deformation[6], shift to lower frequency region with decreased intensity in the spectra of the complexes. A strong band at 1510 cm^{-1} in benzidine, which can easily be assigned to ring vibrations, is slightly shifted to lower frequency in the spectra of metal complexes. The medium intensity band at 1350 cm^{-1} in the ligand observed by Rahman *et al.*[7] could not be observed because it was masked by the strong band of nujol at 1385 cm^{-1}. A strong band at 1275 cm^{-1} in the spectrum of benzidine assignable to νC—N decreases both in frequency and intensity on complex formation. The NH_2 rocking occurs between 815 and 830 cm^{-1}. The νV—O band appears at 1020 cm^{-1} in the vanadyl complex[8,9] and there is a weak absorption in the range 960-980 cm^{-1} which may be assigned to coordinated sulphate, for which ν_1 occurs at 970 cm^{-1} in $[Co(NH_3)_5SO_4]Br$ (ref. 10).

The magnetic moments of 1·73, 5·76 and 6·06 BM respectively for the vanadyl, Mn(II) and Fe(III) complexes are normal. Syamal[4] has reported a value of 5·8-5·9 BM, a sextet ground state and a tetrahedral structure for the Mn(II) complex. The magnetic moment of 4·27 BM for Co(II) complex signifies a tetrahedral structure and probably unusually large orbital contribution[11]. The Ni(II) complex being diamagnetic, may be assigned a square-planar structure. Zn(II), Cd(II) and Hg(II) complexes are also diamagnetic, as expected. The values of 1·92 and 1·95 BM for the Cu(II) and Ru(III) complexes are in agreement with the values reported for other complexes[12-14] of these metal ions. The Rh(III), Pd(II) and Pt(IV) are diamagnetic which is in agreement with the general behaviour of the complexes of these ions[15-19]. The gold complex is diamagnetic and may, therefore, have a square-planar structure.

The comparable molar conductances of $MnCl_2$, $CoCl_2$, $NiCl_2$, $CuCl_2$, $RuCl_3$, $RhCl_3$ and $AuCl_3$ with the corresponding benzidine complexes in dimethyl sulphoxide indicate that the chloride is not coordinated in the complexes of these metal ions. However, the two Cl^- ions may be coordinated in the solid state rendering Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) tetracoordinate and Ru(III), Rh(III), Au(III), Pd(II) and Pt(IV) hexacoordinate. This finds support from the magnetic data of the complexes. The vanadyl sulphate complex likewise is tetracoordinate with sulphate radical probably inside the coordination sphere. In all these complexes benzidine behaves as a bidentate ligand DMSO which is used as the solvent in the conductance studies may enter the coordination sphere by displacing the chlorides.

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LANTHANIDE COMPLEXES OF BIS-SALICYLALDEHYDE-*o*-DIANISIDINE

M. SHAMEEM ANSARI and NASEER AHMAD

(Department of Chemistry, Aligarh Muslim University, Aligarh, U. P. India)

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M. SHAMEEM ANSARI and NASEER AHMAD

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The complexes formed by the interaction of trivalent lanthanide (except Pm and Lu), and yttrium ions with bis-salicylaldehyde-dianisidine were prepared and characterized by elemental analysis, m.p., thermogravimetric analysis, magnetic moments, molar conductance and infrared spectra. The complexes are of the composition:

$$Ln(C_{28}H_{22}N_2O_4)Cl \cdot 3H_2O$$

The molar conductances of these complexes are in the range for 1 : 1 electrolytes and this indicates that the chloride ion is in the outer coordination sphere. The magnetic moments, when plotted against the atomic number give the usual unequal double-humped curve. The thermogram shows that one of the three water molecules in the europium and ytterbium complexes is outside the coordination sphere and thus these metals are hexacoordinated, whereas the La, Pr, Tb and Ho are heptacoordinated. The difference between the total observed weight loss and the weight loss calculated for the formation of the metal increases with the decrease in the size of the lanthanide ion probably because the complex species undergo volatilization on heating at various stages leaving lesser amount of metal than required on stoichiometric considerations. I. R. spectrum is discussed.

Only a few papers appeared so far on the lanthanide(III) complexes of Schiff bases [1–2]. In a previous communication [3] we have reported the synthesis and characterization of yttrium(III) and lanthanide(III) complexes of the tetradentate Schiff base obtained from vanillin and benzidine.

The present communication deals with the preparation of the lanthanide(III) and yttrium(III) complexes with the Schiff base obtained from salicylaldehyde and *o*-dianisidine. They were subjected to elemental and thermogravimetric analyses, their melting points, magnetic moments and mole conductances determined and infrared spectra taken.

Experimental

Lanthanide trichloride (Leico Chemicals, U. S. A.) and yttrium trichloride (E. Merck, Germany) were used to prepare the complexes. The Schiff base, bis-salicylaldehyde-*o*-dianisidine was obtained by the condensation of salicyaldehyde and *o*-dianisidine in the mole ratio of 2 : 1 in ethanol and recrystallized from the same solvent as large needles.

The complexes were prepared by the reaction of the the Schiff base with rare-earth chlorides in hot ethanolic solution in 1 : 1 mole ratio. When the two solutions were mixed, colour changed from orange to brown and on further heating a granular precipitate separated. The precipitate was separated by centrifugation, washed several times with ethanol and finally with ether and dried in vacuo.

The compounds were subjected to elemental analyses for carbon, hydrogen and nitrogen at the microanalytical section of this department.

The thermograms of six complexes were recorded between room temperature and 800 °C and the percent loss was plotted against temperature.

The magnetic measurements were made with the help of Gouy balance at room temperature. Diamagnetic corrections for the ligand were applied and the values of magnetic moments were plotted versus the atomic numbers of the rare-earths.

The mole conductances of 10^{-3} *M* solutions of the complexes in dimethyl sulphoxide were measured with a Philips PR 9500 conductivity bridge, using a dip type cell. The infrared spectra of the complexes were recorded in the range of 4000—600 cm^{-1} in KBr disc with an Infracord model 137B.

Results and discussion

Elemental analysis shows that the rare-earth and yttrium ions react with bis-salicylaldehyde-*o*-dianisidine in 1 : 1 mole ratio and that the general formula for these complexes is

$$MLCl \cdot 3H_2O \quad \text{or} \quad C_{28}H_{22}N_2O_4ClM \cdot 3H_2O$$

where M = lanthanide (except Pm and Lu) and yttrium ions,

L = bis-salicylaldehyde-*o*-dianisidine—2H.

The mole conductances of these complexes at 10^{-3} *M* concentrations in dimethyl sulphoxide range between 41.39 and 53.12 $Ohm^{-1}cm^2mole^{-1}$. BROOMHEAD and KANE-MAGUIRE [4] reported 24 and 27 $Ohm^{-1}cm^2mole^{-1}$ molar conductances for ethylenediamine complexes of cobalt(III) and ruthenium(III) in dimethyl sulphoxide. On this basis we believe that bis-salicylaldehyde-*o* dianisidine complexes of rare-earths and yttrium are 1 : 1 electrolytes. This shows that the chloride is outside the coordination sphere.

The magnetic moments of the rare-earths, when plotted against their atomic numbers, show the usual double-humped curve.

The thermograms of La, Pr, Eu, Tb, Ho and Yb complexes show peculiar features. The removal of the first, second and third water molecules becomes more facile with increase in atomic number of the lanthanide ions up to ytterbium. The first water molecule is removed at about 100 °C or above, except in the case of europium and ytterbium. The other water molecules are removed at higher temperatures. The three water molecules are thus coordinated to the metal ions, except in the case of europium and ytterbium where one water molecule seems to be present in the crystal lattice. In these complexes the metal ions are heptacoordinated with the exception of europium and yttrium which are hexacoordinated. The observed total percent weight loss is greater than the theoretically calculated weight loss. This difference increases with the decrease in the size of the rare-earth ion. The explanation lies in the fact that the volatility of the complex species left after the removal of the three

Table I

Elemental analyses and some characteristic data

Compounds	% C	% H	% N	M P °C	μ_{eff} (B. M.)	Molar cond $Ohm^{-1}cm^2$ $mole^{-1}$
1. $LaLCl3H_2O$	(49.55)	(4.12)	(4.12)	245	Diamag.	41.39
	50.29	4.24	4.28			
2. $CeLCl3H_2O$	(49.45)	(4.11)	(4.11)	235—40	3.1	43.35
	50.21	4.30	4.22			
3. $PrLCl3H_2O$	(49.41)	(4.11)	(4.11)	275	3.85	47.17
	49.92	4.18	4.19			
4. $NdLCl3H_2O$	(49.14)	(4.09)	(4.09)	242—46	3.66	48.45
	49.75	4.23	4.11			
5. $SmLCl3H_2O$	(49.02)	(4.06)	(4.06)	250	1.82	50.15
	50.01	4.30	4.21			
6. $EuLCl3H_2O$	(48.62)	(4.05)	(4.05)	245	3.68	49.3
	49.11	4.28	4.21			
7. $GdLCl3H_2O$	(48.18)	(4.01)	(4.01)	255	8.22	45.9
	49.03	4.26	4.18			
8. $TbLCl3H_2O$	(48.12)	(4.01)	(4.01)	260	10.12	50.15
	48.91	4.35	4.30			
9. $DyLCl3H_2O$	(47.98)	(3.98)	(3.98)	255	10.71	48.45
	48.88	3.79	4.18			
10. $HoLCl3H_2O$	(47.56)	(3.96)	(3.96)	260	10.68	53.12
	48.65	4.11	3.77			
11. $ErLCl3H_2O$	(47.45)	(3.95)	(3.95)	260	9.59	48.45
	48.51	4.15	4.08			
12. $TmLCl3H_2O$	(47.45)	(3.95)	(3.95)	258	7.9	48.45
	47.25	4.10	3.99			
13. $YbLCl3H_2O$	(47.17)	(3.93)	(3.93)	260	4.85	48.45
	48.09	4.08	4.00			
14. $YLCl3H_2O$	(53.49)	(4.45)	(4.45)	255		42.5
	54.14	4.70	4.55			

Calculated values are given in parentheses. L = bis-salicylaldehyde-*o*-dianisidine.

water molecules and some portion of the ligand increase with a decrease in the size of the cation, so that less metal is deposited than expected on stoichiometric consideration (see Table II).

Bis-salicylaldehyde-*o*-dianisidine has medium and broad bands at 3571 and 3030 cm^{-1} which may be due to the antisymmetric OH stretching mode, and a strong band at 1613 cm^{-1} which may be due to C=N stretching vibra-

Table II

Compounds	Removal of 1 st water molecule			Removal of 2nd water molecule		
	Wt. loss %			Wt. loss %		
	Theor.	Obs.	Temp. °C	Theor.	Obs.	Temp. °C
$LaLCl3H_2O$	2.65	2.7	148	5.30	5.3	165
$PrLCl3H_2O$	2.64	2.7	125	5.28	5.3	161
$EuLCl3H_2O$	2.62	2.7	86	5.20	5.2	150
$TbLCl3H_2O$	2.58	2.6	110	5.16	5.2	145
$HoLCl3H_2O$	2.55	2.6	142	5.10	5.1	159
$YbLCl3H_2O$	2.52	2.5	80	5.04	5.0	157

Compounds	Removal of 3rd molecule			Metal formation		
	Wt. loss %			Wt. loss %		
	Theor.	Obs.	Temp. °C	Theor.	Obs.	Temp. °C
$LaLCl3H_2O$	7.95	8.0	178	79.58	82.0	591
$PrLCl3H_2O$	7.92	8.0	176	79.3	85.3	601
$EuLCl3H_2O$	7.80	7.8	165	78.91	95.5	562
$TbLCl3H_2O$	7.74	7.75	159	77.4	92.5	571
$HoLCl3H_2O$	7.65	7.70	171	76.4	95.5	568
$YbLCl3H_2O$	7.56	7.70	171	75.12	96.5	580

tions. TANDON *et al.* [6] have assigned O=C C=N stretching frequency bands at 1605 and 1630 cm^{-1} in the salicylidene-2-hydroxy-*n*-propylamine and bis-salicylidene-ethylenediamine, respectively.

The C=N stretching band shifts to higher frequency (1654 1629 cm^{-1}) on complexation. This shift to higher frequency is in accordance with the observation of BIRADAR and KULKARNI [7] in titanium(IV) salicylidene complex. The antisymmetric OH stretching bands exist in the complexes but slightly decrease in frequency. A medium band appears in the region of 890—880 cm^{-1} in the complexes, which is absent in the i.r. spectrum of the ligand. This band may be due to the coordinated water in the complexes.

Since water molecules are present in the complexes, i.r. spectra cannot be used to reveal whether hydroxyl groups are ionized and co-ordinated. However, elemental analysis, the presence of one chloride, and the proximity of the hydroxyl group to the nitrogen lead us to believe that the phenolic OH coordinates make the complexes heptacoordinate, except perhaps with europium and terbium which are hexacoordinated, as one of the three water molecules in their complexes is lattice water.

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M. Shameem ANSARI
Naseer AHMAD
Department of Chemistry, Aligarh Muslim University, Aligarh, U. P. India.

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METAL–AMINO ACID INTERACTION, II 48

A STUDY OF THE COMPLEX COMPOUNDS OF TRIVALENT RARE EARTHS WITH GLUTAMIC ACID

Omar FAROOQ and Naseer AHMAD

(Inorganic Research Laboratory, Chemistry Department, Aligarh Muslim University, Aligarh, U. P. India)

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The complexes of trivalent rare earths with glutamic acid are reported. The elemental analyses supported the formula $(Glut\text{-}H)_3$ R. E. 3 H_2O (where Glut = glutamic acid and R. E. = trivalent rare earths). Thermogravimetric studies revealed the presence of three coordinated water molecules. The magnetic moments in B. M. give the characteristic unequal double humped curve and infra-red spectra taken in the range between 2.5 and 16 μ in KBr pellets showed the coordination of rare earth ions through the ionized carboxylic group adjacent to the amino group. The comparable molar conductances of the rare earth salts and the complexes in aqueous solutions demonstrated greater ionic bonding between rare earths and amino acids.

Metal protein complexes have emerged as a central problem of bioinorganic chemistry. Amino acids being an integral part of proteins play an important role in the process of isolation and purification of proteins. A number of transition metal–amino acid complexes have been studied mainly with a view to affecting the separation and identification of amino acids [1—6]. The interaction of lanthanides with amino acids has been studied mostly in solution employing various physico-chemical methods [7—10], but very little attention has been paid to their isolation and elucidation of their structure. Recently a detailed study of this aspect of the problem was undertaken by the authors and the complex compounds of trivalent rare-earths with an essential amino acid, L-aspartic acid were reported [11]. The present communication deals with the isolation and characterisation of rare earths with glutamic acid. These studies are based upon elemental analysis, molar conductance, thermogravimetric analysis, i. r., decomposition temperature and magnetic measurement.

Experimental

Freshly precipitated carbonate, prepared from their oxides (A. R. Koch — Light, London), were treated with aqueous solution of glutamic acid (A. R. B. D. H. England) in stoichiometric proportions with a slight excess of the carbonate. The mixture was stirred for an hour, filtered and the filtrate concentrated, mixed with a slight excess of ethanol and left for slow evaporation to obtain crystalline compounds which were dried in vacuum at room temperature for several days over P_2O_5.

The i. r. spectra were taken in the NaCl region in KBr pellets with a Beckman Spectrophotometer, model BK 56 (U. S. A.) between 2.5 and 16 μ. Thermolysis curves were recorded with a Stanton Thermobalance (U. K.) from 25 to 900°C in air with a heating rate of 6° per

minute. The molar conductances were measured with a Philips Conductivity Bridge, model PRI 500 (India) in conjunction with a dip type cell(cell factor 1.48), and the magnetic measurements were carried out at 27°C employing Faraday's method. The analyses for C, H and N were done by the Microanalytical Service I. I. T., Kanpur (India). Rare earths were determined as their oxalates [12]. No melting was observed up to 360°C. These compounds are extremely hygroscopic, they do not dissolve in common organic solvents but have high solubility in water. Table I gives elemental analyses and some characterising data about these compounds.

Results and discussion

Elemental analyses for carbon, hydrogen, nitrogen and rare-earths and thermogravimetric studies supported the formula $M(glut\text{-}H)_3 . 3\ H_2O$. The dehydration occurs between 124 and 205°C in all of these compounds as is evident from 8—9% approximate weight loss. After 205°C, the decomposition of the hydrated compounds starts and leads to the evolution of probably both carbon dioxide and carbon monoxide. The formation of stable oxides of rare-earths starts from around 650°C (La, Pr to Lu except Pm). In the case of cerium glutamate there is direct conversion to stable oxide CeO_2 from about 350°C with a 73% weight loss. In case of yttrium, the formation of Y_2O_3 is complete at 700°C. The removal of water molecules in the range of 125—205°C shows that all the three water molecules are coordinated to metal ions [13].

The magnetic moments in B. M. calculated after applying the diamagnetic correction for glutamic acid and the water molecules give the characteristic unequal double humped curve [14]. The molar conductances of $2.0 \times \times 10^{-4}$ *M* aqueous solutions of these compounds were of the order of 0.38 ± 0.1 mhos cm^2 and those of the corresponding trichlorides of rare earths more or less of the same magnitude and order but about 2.7 times higher than the corresponding glutamates. This is perhaps due to the ionic bonding between the metal and the amino acid. The slightly larger value for the rare earth salts might be due to the high ionic mobility of the chlorides as compared to that of large amino acid anions.

The peaks on the i. r. spectra of these complexes were compared with those of glutamic acid. The bands which throw some light on active coordinating abilities of amino acids are NH_3^+ sym and asym [15], COO^- sym and asym [16], and CN stretchings [17]. The NH_3^+ asym stretching vibrations of free glutamic acid appear as medium intensity bands at 1620 and 1520 cm^{-1}, respectively. On complexation, these bands disappeared. The COO^- sym vibration which occurs at 1420 cm^{-1} as medium intensity band in free acid is lowered by 15—20 cm^{-1} as a strong band on complexation in all the cases. However, the COO^- asym band occurring at 1640 cm^{-1} as medium intensity is of reduced intensity and appears in the form of a shoulder at 1635—1630 cm^{-1} in these compounds. The CN stretching vibrations present as a medium sharp intensity band at 920 cm^{-1} in glutamic acid showed a lowering of 30 to 50 cm^{-1} in the complexes. It is quite difficult to select between COO^- and NH_3^+ stretchings

Table I

Some characterising data

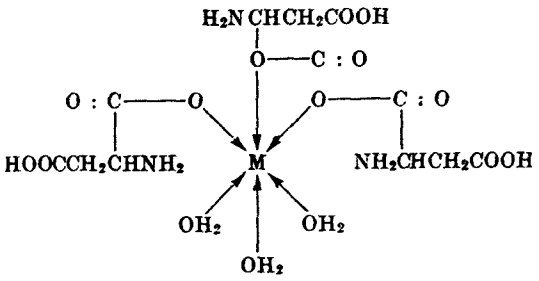
Compound	Carbon	Hydrogen	Nitrogen	Rare earth	Magnetic moment (B. M.)	Molar conductance	Colour
$Y(Glut)_3{}^*3H_2O$	30.98 (30.90)	5.16 (5.20)	7.23 (7.20)	15.13 (15.20)	Diamag	0.37	Light yellow
$La(Glut)_33H_2O$	28.95 (28.40)	4.76 (4.81)	6.66 (6.72)	22.08 (22.15)	-do-	0.38	White
$Ce(Glut)_33H_2O$	28.47 (28.50)	4.77 (4.90)	6.65 (6.73)	22.15 (22.02)	1.98	0.38	Light pink
$Pr(Glut)_33H_2O$	28.44 (28.56)	4.74 (4.82)	6.64 (6.70)	22.12 (22.20)	3.42	0.38	White
$Nd(Glut)_33H_2O$	28.27 (28.32)	4.71 (4.32)	6.60 (6.70)	6.60 (6.70)	3.54	0.37	Pinkish white
$Sm(Glut)_33H_2O$	28.02 (28.00)	4.67 (4.70)	6.54 (6.66)	22.45 (22.50)	1.90	0.37	Dirty white
$Eu(Glut)_33H_2O$	27.96 (28.01)	4.66 (4.60)	6.52 (6.50)	23.59 (23.70)	3.78	0.37	White
$Gd(Glut)_33H_2O$	27.73 (22.90)	4.62 (4.68)	6.46 (6.42)	24.22 (24.30)	7.80	0.37	Dirty white
$Tb(Glut)_33H_2O$	27.66 (27.70)	4.61 (4.59)	6.45 (6.49)	24.42 (24.51)	9.38	0.38	White
$Dy(Glut)_33H_2O$	27.51 (27.60)	4.58 (4.68)	6.42 (6.48)	24.83 (24.73)	10.18	0.39	White
$Ho(Glut)_33H_2O$	27.40 (27.50)	4.57 (4.67)	6.39 (6.40)	25.10 (25.19)	10.22	0.38	White
$Er(Glut)_33H_2O$	27.31 (27.40)	4.56 (4.60)	6.37 (6.40)	25.45 (25.55)	9.25	0.39	White
$Tm(Glut)_33H_2O$	27.22 (27.30)	4.54 (4.58)	6.35 (6.39)	25.54 (25.43)	7.58	0.39	White
$Yb(Glut)_33H_2O$	27.07 (27.17)	4.51 (4.55)	6.31 (6.38)	26.01 (26.20)	4.50	0.39	White
$Lu(Glut)_33H_2O$	26.99 (27.02)	4.49 (4.52)	6.29 (6.34)	26.16 (26.24)	Diamag	0.37	White

* Glut = Glutamic acid-H, $C_5H_8O_4N-H$.
The observed values are given in parentheses.

as pertinent sites of coordination but generally in amino acids, coordination through COO^- groups takes place with normal change in the NH_3^+ stretching vibrations [18]. Moreover, glutamic acid being a dicarboxylic acid is prone to lose a proton from COOH (pKa $\sim$ 4.0) rather than NH_3^+ group (pKa$\sim$9.80).

In view of the above facts, it may safely be assumed that glutamic acid retained its 'zwitter ion' character in its complexes and the possibility of its

coordination through nitrogen is ruled out. The following structure may be assigned



where M = rare earth ion.

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Omar FAROOQ, Naseer AHMAD } Inorganic Research Laboratory, Chemistry Department, Aligarh Muslim University, Aligarh/U. P. India.

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Studies on lanthanide complexes of bis vanillin-benzidine

49

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VERY little work has been done on lanthanide(III) complexes of Schiff bases Yamada *et al* [1] have synthesised the lanthanide(III) chelates with various Schiff bases derived from salicylaldehyde and different amines Datt and Nag[2] have reported a new series of rare-earth metal chelates with tetradentate Schiff bases obtained from salicylaldehyde and ethylenediamine and orthophenylenediamine and characterised them by their thermal analyses and IR spectra

The present communication deals with the preparation of yttrium(III) and lanthanide(III) complexes with bis vanillin-benzidine and their characterisation by elemental analyses, m p 's, thermograms, magnetic moments, molar conductances and IR spectra

EXPERIMENTAL

Rare-earth halides (Leico chemicals, U S A) and YCl_3 (E Merck, Germany) were used to prepare the complexes without further purification The Schiff base bis vanillin-benzidine was obtained by the condensation of vanillin (Bush Boake Allen, London) and benzidine (Renal, Hungary) in stoichiometric quantities (2 1 molar ratio) in ethanol, and the precipitate obtained was separated and dried *in vacuo*

The complexes were prepared by mixing the rare-earth chlorides and the Schiff base in the ratio of 1 1 in ethanol when the colour changes from yellow to reddish brown and a reddish precipitate settles on heating The precipitate was centrifuged, washed several times with ethanol and finally with ether and dried *in vacuo*

The compounds were analysed for carbon, hydrogen and nitrogen and the chloride estimated as silver chloride

The thermograms were recorded between room temperature and 500°C and the percent loss was plotted vs temperature Melting was accompanied with decomposition at temperatures above 300°C The magnetic measurements were made with a Gouy balance at room temperature Diamagnetic corrections were applied for the ligand and the values of magnetic moments were plotted vs the atomic numbers of the rare-earths

The molar conductances of 10^{-3}M solutions of the complexes in dimethyl sulphoxide were measured on a Philips PR 9500 conductivity bridge using a dip type cell

The IR spectra of the complexes were recorded with an infracord model 137B in the range of 600–400 cm^{-1} in KBr phase

RESULTS AND DISCUSSION

Analyses (Table 1) of the products of reaction of bis vanillin-benzidine with trivalent yttrium and rare-earth ions show that interaction occurs in 1 1 molar ratio giving products of composition, $C_{28}H_{22}N_2O_4ClM\cdot 3H_2O$ This involves the ionisation of the phenolic hydroxyl group on each of the aldehydes in the ligand and the association of three water molecules in the complex

The magnetic moments of these complexes show the usual double humped curve when plotted vs the atomic numbers of the rare earths The molar conductances at 10^{-3}M concentration in DMSO range between 51 1 and 69 1 Ω^{-1}cm^{2}mole^{-1} Greenwood *et al* [3] reported 50–70 Ω^{-1}cm mole^{-1} as the range for the 1 1 electrolytes in this solvent Ames and Sears[4] computed ranges 70–90, 60–90, 70–80, 55–75, 55–80, and 85 downwards for 1 1 complexes and on this basis suggested that a reasonable range is 65–90 Ω^{-1}cm^{2}mole^{-1} for 1 1 electrolytes This suggests that the complexes are 1 1 electrolytes

The thermogram for the praseodymium complex shows a weight loss of about 2 7% (theoretical weight loss 2 64% for one water molecule) at 70°C and a final weight loss of 8% (theoretical weight loss 7 9% for $3H_2O$) This suggests that out of the three water molecules one is lattice water and two are coordinated to the metal as they are removed only at temperatures above 100°C (*vide* Table 1 for weight losses in other complexes)

The IR spectra of these complexes show medium intensity bands at 3300 and 3400 cm^{-1} region which must be due to lattice water In general lattice water absorbs at 3550–3200 cm (antisymmetric and OH stretching modes), and at 1630–1600 cm (HOH bending modes) The bending mode of lattice water which was expected in the 1630–1600 cm^{-1} region in these complexes was not observed because there are other strong absorptions in this region The bands at 3400 and 3300 cm corroborate our results of TGA, that one water molecule is present as lattice water

A clear band in the region 825–833 cm^{-1} is due to the rocking mode of water activated by coordination to the metal Fujita *et al* [5] have examined the IR spectra of typical aquo complexes and found bands characteristic of coordination water near 795 875, 1012 and 965 cm^{-1} Sartori *et al* [6] have calculated the vibrational frequencies of coordinated water and found the rocking, wagging and the metal-oxygen stretching vibrations at 900 768 and 673 cm^{-1}

In bis vanillin benzidine the stretching frequency of the C=N band appears at 1625 cm^{-1} Another strong band at 1425 cm^{-1} is the C–O stretching frequency of the phenolic part of the vanillin The C–N absorption frequency has been reported at 1630[7], 1661 and 1630[8], 1650 and 1660[9], and 1610[10] by various workers Biradar and Kulkarni[11] have assigned the strong bands at 1620 and 1610 cm^{-1} to C–N stretching in Schiff base and found that this is shifted to higher frequency, i e 1650 and 1630 cm^{-1} on complexation with titanium(IV)

Both these strong bands (1625 cm^{-1} for C N and 1425 cm for C–O) are shifted to higher frequencies on complexation with trivalent yttrium and rare earth ions

The OH deformation mode probably occurs at 1274 cm in bis vanillin benzidine This decreases in intensity and in some cases disappears on complexation

This is a proof that coordination has taken place through the oxygens of the two phenolic hydroxyl groups and the nitrogens of the two imine groups The complexes can be represented by the formula

[M(bis vanillin benzidine)2H$_2$O]Cl H O

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Department of Chemistry
Aligarh Muslim University
Aligarh
U P , India

M SHAMFEM ANSARI
NASEER AHMAD

Table 1. Analyses and some characterising data

	Compounds		% C	% H	% N	% Cl	Λ_M Ohm^{-1}Cm^{2}mole^{-1}	Mag.moment	$1H_2O$	Temp.	$3H_2O$	Temp
1.	La, L. Cl. $3H_2O$	Calcd	49.55	4.12	4.12	5.22		(B.M.)	2.6%		7.95%	
		Found	50.21	4.19	4.13	5.30	53.4	Diamag.	2.5%	65°C	8%	145°C
2.	Ce. L. Cl. $3H_2O$	Calcd	49.45	4.11	4.11	5.21						
		Found	50.11	4.35	4.28	5.28	58.7	2.45				
3.	Pr. L. Cl. $3H_2O$	Calcd	49.41	4.11	4.11	5.21			2.69%		7.9%	
		Found	50.02	4.15	4.36	5.15	60.7	3.5	2.7%	70°C	8%	115°C
4.	Nd. L. Cl. $3H_2O$	Calcd	49.14	4.09	4.09	5.18						
		Found	49.62	4.25	4.26	5.13	68.9	3.41				
5.	Sm. L. Cl. $3H_2O$	Calcd	49.02	4.06	4.06	5.12			2.6%		7.8%	
		Found	49.56	4.17	4.09	5.10	57.4	2.3	2.7%	80°C	7%	115°C
6.	Eu. L. Cl. $3H_2O$	Calcd	48.62	4.05	4.05							
		Found	49.13	4.13	4.18		69.1	3.6				
7.	Gd. L. Cl. $3H_2O$	Calcd	48.18	4.01	4.01				2.58%	70°C	7.73%	150°C
		Found	48.71	4.21	4.19		68.9	7.8	3%		8%	
8.	Tb. L. Cl. $3H_2O$	Calcd	48.12	4.01	4.01				2.58%	80°C	7.7%	160°C
		Found	48.61	4.12	4.15		69.0	9.8	3%		8%	
9.	Dy. L. Cl. $3H_2O$	Calcd	47.83	3.98	3.98				2.5%	90°C	7.69%	170°C
		Found	48.25	4.08	4.11		65.5	10.35	2.5%		8%	
10.	Ho. L. Cl. $3H_2O$	Calcd	47.56	3.96	3.96							
		Found	48.20	4.01	4.08		68.9	10.2				
11.	Er. L. Cl. $3H_2O$	Calcd	47.45	3.95	3.95							
		Found	48.12	4.02	4.12		60.7	9.7				
12.	Tm. L. Cl. $3H_2O$	Calcd	47.45	3.95	3.95				2.54%		7.6%	
		Found	48.01	3.99	4.10		56.6	7.4	2.6%	65°C	7%	125°C
13.	Yb. L. Cl. $3H_2O$	Calcd	47.17	3.93	3.93			4.39	2.52%	50°C	7.58%	110°C
		Found	47.73	3.97	4.11		60.7		3%		8%	
14.	Y. L. Cl. $3H_2O$	Calcd	53.49	4.45	4.45							
		Found	54.15	4.71	4.22		53.1	Diamag.				

L represents bis vanillin-benzidine.

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Interaction of metal ions with uridine triphosphate

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WE HAVE reported earlier[1] on the metal chelates of guanosine triphosphate (GTP), inosine triphosphate (ITP) and the corresponding thermodynamic quantities with bivalent metal ions In a recent publication[2] the metal chelates of cytidine triphosphate (CTP) were also reported The present paper extends the work to uridine triphosphate (UTP) Although the metal complexes of adenine nucleotides have been the subject of several studies[3–7], complexes of uridine triphosphate (UTP) have not been thoroughly investigated A previous investigation by Wallas[8] was restricted to the complexes of UTP with CO(II), Mg(II), Mn(II) and Ca(II) by an ion exchange method Consequently, detailed physico chemical studies on the complex formation of UTP with bivalent metal ions have been carried out for the first time

EXPERIMENTAL

Reagents Uridine triphosphate[Schwarz Mann Research Laboratory (U S A)] was used as the sodium salt Fresh solid ligand was weighed out for each titration to avoid the possibility of hydrolysis if a stock solution were employed All transition and alkaline earth metal ions were of AnalaR grade and the metal ions were standardised volumetrically by EDTA titration as outlined by Schwarzenbach[9] Carbonate-free sodium hydroxide was prepared and standardised by titration with potassium hydrogen phthalate

Procedure Potentiometric titrations of the ligand were done with standard sodium hydroxide solution in the absence and in the presence of the metal ion being investigated at 35 ± 0 1°C The ionic strength was maintained constant by using 0 10 M(KNO_3) as the supporting electrolyte and relatively low concentrations of ligand and metal ion A stream of nitrogen was passed through the solution to exclude atmospheric carbon dioxide

A Beckmann Model "G" pH meter with glass and calomel electrodes was used to determine hydrogen ion concentration The electrode system was calibrated by direct titration of acetic acid and the observed pH meter reading was compared with the actual hydrogen ion concentration determined from the pK values of acetic acid at 35°C as tabulated by Harned and Owen[10] The pH regions below 3 5 and above 10 5 were calibrated by measurements in HCl and NaOH solutions, respectively

Calculations The acid dissociation constants of the mono sodium salt of UTP (H_3L) are related to the dissociation equilibrium as follows

$$H_3L \overset{K_a K_{2a}}{\rightleftharpoons} HL^{3-} + 2H \quad (1)$$

$$HL^{3-} \overset{K_{3a}}{\rightleftharpoons} L^{4-} + H \quad (2)$$

The constants pK_a, pK_{2a} were calculated by the graphical method of Schwarzenbach and Martell[11] and pK_{3a} by the usual algebraic method

To determine the stability constants of the normal 1 1 complexes formed during a titration of 1 1 mixture of ligand and metal ion, the following equations were used

$$M^{2+} + L^{4-} \overset{K_1}{\rightleftharpoons} ML^{2-} \quad (3)$$

Related equilibria may be described as

$$M^{2-} + H_3L \rightleftharpoons ML^{2-} + 3H \quad (4)$$

The following expressions may be written *assuming that a normal 1 1 complex species is formed in the buffer region between* $a = 0$ *and* $a = 3$ If T_L represents the total concentration of various ligand species and T_M that of all metal species then

$$T_L = [H_3L] + [H_2L^{2-}] + [HL^{3-}] + [L^{4-}] + [ML^{2-}] \quad (5)$$

$$T_M = [M^{2+}] + [ML^{2-}] \quad (6)$$

The total amount of titrable hydrogen

$$[H^+] = [H_2L^{2-}] + 2[HL^{3-}] + 3[L^{4-}] + 3[ML] - aT_L + [OH] \quad (7)$$

where a represents, moles of base added per mole of UTP present Solving we have for $[L^{4-}]$

$$[L^{4-}] = \frac{\alpha}{X} \quad (8)$$

where

$$\alpha = (3 - a)T_L - [H] + [OH]$$

and

$$X = \frac{3[H]^3}{K_a K_{2a} K_{3a}} + \frac{2[H]^2}{K_{2a} K_{3a}} + \frac{[H]}{K_{3a}}$$

Equation (8) is solved for $[L^{4-}]$ and may be related to $[M]$ by the expression

$$[M] - [L^{4-}]Y$$

where

$$Y = \frac{[H]^3}{K_a K_{2a} K_{3a}} + \frac{[H]^2}{K_{2a} K_{3a}} + \frac{[H]}{K_{3a}} + 1$$

The value of $[M]$ and $[L^{4-}]$ may then be used with eqns (5)–(7) to calculate the unknowns in eqn (3) and the value of K_1 determined

RESULTS

Determination of pK *values of UTP* The potentiometric titration curves of UTP (H_3L) shown in Fig 2 indicate a simultaneous dissociation of two protons from the ligand between

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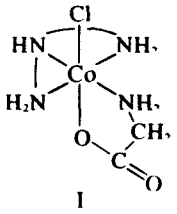
25°C and $I = 0.1$ M. The κ-isomer undergoes base hydrolysis some 4×10^3 times faster than the π isomer. Both the ω- and π isomers have the dien ligand in a *fac*-configuration while the ligand is *mer* in the κ-isomer. The results suggest that complexes with a *mer* dien configuration undergo base hydrolysis some 10^3 times faster than analogous complexes with a *fac*-configuration. In order to provide additional evidence for this conclusion we have also studied the base hydrolysis of *trans*(O,Cl)-[CoCl(gly)(dien)]$^{2+}$



I

The structure of this complex (I) has recently been established by X-ray crystallography[8]. In this case $k_{OH} = 1.3 \times 10^4$ M^{-1} s^{-1} at 25°C and $I = 0.1$ M (Table 1). Base hydrolysis rates can therefore be of value in assigning configurations to Codien complexes.

The base hydrolysis of cobalt(III) complexes is generally accepted to occur by an SN_1CB mechanism[9]. Nordmeyer[10] has suggested that in the base hydrolysis of cobalt(III) complexes by an SN_1CB mechanism the labile conjugate base is that with the amido group *cis* to the leaving group. The secondary nitrogen proton of the dien ligand is the most acidic site and thus if the ionisation of the most acidic proton leads to the formation of the active amido species (which may not necessarily be the case) the π-isomer should be more active in base hydrolysis than the ω-isomer, as is observed.

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Chemistry Department R. W. HAY
University of Stirling
Stirling FK9 4LA
Scotland

Chemistry Department K. B. NOLAN
University of Surrey
Guildford GU2 5XH
Surrey
England

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Studies on mixed ligand complexes of silver(I) halides—I. Interaction of silver(I) thiourea, naphthyl and diphenyl thiourea halides with pyridine, 2,2′-dipyridyl and 1,10-phenanthroline

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SILVER(I) forms complexes with thiourea[1–4] and also with the heterocyclic amines pyridine[5], orthophenanthroline[6] and 2,2′-dipyridyl. It seemed possible therefore that mixed ligand complexes of silver(I) with thioureas and heterocyclic amines might be prepared.

The present communication reports Ag(S tu)X and Ag(S tu)AM X complexes where S tu = thiourea, naphthylthiourea or diphenylthiourea, AM = pyridine, 2,2′-dipyridyl or *o*-phenanthroline and X = chloride, bromide or iodide. Thirty three new complexes have been characterised by elemental analyses for carbon, hydrogen nitrogen and silver and by melting points, molar conductances in acetone and IR spectra.

EXPERIMENTAL

Thiourea, α-naphthylthiourea, diphenylthiourea, pyridine, 2,2′-dipyridyl and *o*-phenanthroline (B.D.H. reagent grade) and freshly precipitated silver halides were used to prepare the complexes. To a well stirred suspension of the silver halide (0.5×10^{-2} mole) in acetone (5 ml), thiourea solution (0.1 M) was added in small portions till only a small amount of silver halide was left undissolved. The mixture was heated on a water bath for about half an hour, filtered, and the clear solution allowed to crystallise. The crystals were dried *in vacuo*.

For the preparation of the mixed ligand complexes, 25 ml of a 0.1 M solution of the silver halide thiourea complex was mixed with pyridine (1:1 molar ratio), heated on a water bath for 5 min, filtered, and left to crystallise. The crystals were then washed with a small amount of acetone and dried *in vacuo*. The mixed ligand complexes of diphenylthiourea silver(I) halides with pyridine could not be isolated.

The complexes were microanalysed for carbon, hydrogen and nitrogen and the percentage of silver was determined by heating a weighed amount of the complex and weighing the residue as silver oxide. The results of chemical analyses are given in Table 1.

The molar conductances of the complexes at 10^{-3} M concentration in acetone were determined with a PR 9500 Philips Conductivity Bridge and a dip type cell. The IR spectra were taken in KBr discs in the NaCl region using a Perkin Elmer infracord model 137B (Table 2).

RESULTS AND DISCUSSION

Elemental analyses for carbon, hydrogen, nitrogen and silver yield the following formula for the complexes

Ag(S tu)AM X

Linear 2 coordinate silver(I) complexes are common. The molar conductance of these complexes at 10^{-3} M in acetone are in the range of 3.4–22.6, 6.42–20.74 and 3.89–12.45 ohm^{-1} cm^2 mole^{-1} for the thiourea, naphthyl thiourea and diphenyl thiourea complexes respectively. Molar conductances at this concentration in acetone are generally 100–140, 160–200, about 270 and about 360 ohm^{-1} cm^2 mole^{-1} for 1:1, 2:1, 3:1 and 4:1 electrolytes[7]. It may be concluded that these complexes are non-electrolytes.

Table 1 Elemental analyses and some characterising data

Sample No	Complexes		Metal %	C %	H %	N %	M Pt (°C)	Colour	Λ_m Ohm^{-1} cm^2 mole^{-1}
1	AgN_2H_4CSCl	Ag(tu)Cl	49 15 (48 90)	5 47 (5 39)	1 82 (1 90)	12 75 (12 72)	156	Colourless	5 7
2	$AgC_6H_9N_3SCl$	Ag(tu)(py)Cl	(35 91)	(23 97)	(3 24)	(14 25)	188	Light brown	8 2
3	$AgC_{11}H_{12}N_4SCl$	Ag(tu)(dipy)Cl	28 74 (28 82)	35 17 (35 48)	3 19 (3 25)	14 90 (14 54)	*145*	*Pink*	*7 4*
4	$AgC_{13}H_{12}N_4SCl$	Ag(tu)(ophen)Cl	27 01 (27 83)	39 06 (39 04)	3 00 (3 28)	14 02 (14 14)	187	Light pink	10 3
5	AgN_2H_4CSBr	Ag(tu)Br	40 87 (40 68)	4 54 (4 68)	1 51 (1 67)	10 64 (10 54)	146	Colourless	4 1
6	$AgC_6H_9N_3SBr$	Ag(tu)(py)Br	31 45 (31 28)	20 99 (20 84)	2 62 (2 64)	12 24 (12 24)	161	Light pink	22 6
7	$AgC_{11}H_{12}N_4SBr$	Ag(tu)(dipy)Br	25 68 (26 00)	31 42 (31 64)	2 85 (2 98)	13 33 (13 32)	174	Light pink	20 4
8	$AgC_{13}H_{12}N_4SBr$	Ag(tu)(ophen)Br	24 30 (24 18)	35 15 (35 92)	2 70 (2 64)	12 61 (12 12)	205	Pink	13 3
9	AgN_2H_4CSI	Ag(tu)I	34 70 (34 28)	3 86 (3 92)	1 28 (Below 1%)	9 00 (9 16)	153	Blackish white	3 4
10	$AgC_6H_9N_3SI$	Ag(tu)(py)I	27 66 (27 48)	18 46 (18 88)	2 30 (2 45)	10 77 (11 23)	131	Brown	17 1
11	$AgC_{11}H_{12}N_4SI$	Ag(tu)(dipy)I	23 00 (22 82)	28 26 (27 86)	2 57 (2 84)	11 99 (12 12)	181	Pale yellow	13 5
12	$AgC_{13}H_{12}N_4SI$	Ag(tu)(ophen)I	21 97 (21 19)	31 76 (31 68)	2 44 (2 46)	11 41 (11 46)	198	Light yellow	14 8
13	$AgC_{11}H_{10}N_2SCl$	Ag(Ntu)Cl	31 23 (30 82)	38 22 (38 17)	2 89 (2 88)	9 09 (8 24)	210	White	20 7
14	$AgC_{16}H_{15}N_3SCl$	Ag(Ntu)(py)Cl	25 41 (25 40)	45 22 (45 64)	3 53 (3 86)	9 89 (10 12)	202	White	13 3
15	$AgC_{21}H_{18}N_4SCl$	Ag(Ntu)(dipy)Cl	21 51 (20 97)	50 24 (50 82)	3 58 (3 56)	11 16 (11 28)	198	Brown	14 4
16	$AgC_{23}H_{18}N_4SCl$	Ag(Ntu)(ophen)Cl	20 53 (19 92)	52 53 (52 68)	3 42 (3 54)	10 66 (10 62)	185	Dirty white	12 6
17	$AgC_{11}H_{10}N_2SBr$	Ag(Ntu)Br	27 67 (27 82)	33 86 (33 93)	2 56 (2 54)	7 18 (7 11)	104	White	9 84
18	$AgC_{16}H_{15}N_3SBr$	Ag(Ntu)(py)Br	23 10 (23 18)	40 94 (41 28)	3 19 (3 22)	3 95 (8 69)	180	White	12 7
19	$AgC_{21}H_{18}N_4SBr$	Ag(Ntu)(dipy)Br	19 60 (19 68)	46 16 (46 16)	3 29 (3 30)	10 25 (10 28)	120	White	10 8
20	$AgC_{23}H_{18}N_4SBr$	Ag(Ntu)(ophen)Br	18 93 (18 35)	48 44 (48 89)	3 15 (3 12)	9 82 (9 45)	160	Dirthy white	6 4
21	$AgC_{11}H_{10}N_2SI$	Ag(Ntu)I	24 68 (24 92)	30 20 (30 42)	2 28 (1 92)	6 38 (6 73)	135	White	8 5
22	$AgC_{16}H_{15}N_3SI$	Ag(Ntu)(py)I	20 87 (20 76)	37 14 (37 16)	2 90 (2 88)	8 10 (8 20)	210	White	10 1
23	$AgC_{21}H_{18}N_4SI$	Ag(Ntu)(dipy)I	18 16 (18 28)	42 42 (42 64)	3 03 (3 18)	9 42 (9 52)	180	Brownish white	12 5
24	$AgC_{23}H_{18}N_4SI$	Ag(Ntu)(ophen)I	17 48 (17 69)	44 74 (44 28)	2 92 (3 16)	9 07 ((8 86)	182	Yellowish white	8 2
25	$AgC_{13}H_{12}N_2SCl$	Ag(Dtu)Cl	29 03 (30 22)	41 98 (42 19)	3 23 (3 40)	7 53 (7 62)	73	White	4 2
26	$AgC_{23}N_{20}N_4SCl$	Ag(Dtu)(dipy)Cl	20 45 (20 42)	52 32 (52 30)	3 79 (3 81)	10 61 (10 77)	128	Black	12 4
27	$AgC_{25}H_{20}H_4SCl$	Ag(Dtu)(ophen)Cl	19 56 (19 86)	54 41 (54 68)	3 62 (3 82)	10 15 (9 88)	151	Pale yellow	10 3
28	$AgC_{13}H_{12}N_2SBr$	Ag(Dtu)Br	25 9	37 5	3 9	6 7	138	*White*	3 8
29	$AgC_{23}H_{20}N_4SBr$	Ag(Dtu)(dipy)Br	18 86 (19 86)	46 27 (48 38)	3 49 (3 45)	9 79 (9 62)	68	Yellow	4 9
30	$AgC_{25}H_{20}N_4SBr$	Ag(Dtu)(ophen)Br	18 09 (18 86)	50 52 (50 38)	3 35 (3 45)	9 39 (9 22)	174	White	10 1
31	$AgC_{13}H_{12}N_2SI$	Ag(Dtu)I	23 3 (23 1)	33 7 (33 6)	2 6 (2 5)	6 0 (6 1)	120	Blackish white	4 4
32	$AgC_{23}H_{20}N_4SI$	Ag(Dtu)(dipy)I	17 40 (17 42)	46 15 (46 54)	3 22 (3 44)	9 03 (9 28)	—	Yellowish white	8 7
33	$AgC_{25}H_{20}N_4SI$	Ag(Dtu)(ophen)I	16 79 (16 28)	46 67 (46 30)	3 11 (3 14)	8 72 (8 45)	165	Pale yellow	5 7

Observed values are given in parentheses tu, thiourea, Ntu, α-naphtyl thiourea, Dty, diphenyl thiourea, py, pyridine, dipy, 2,2'-dipyridyl, ophen, Orthophenanthroline

Table 2 IR spectra (cm $^{-1}$)

Compound	νCN	νCS
tu	1080	735
Ag(tu)Cl	1085	770
Ag(tu)(py)Cl	1090	725
Ag(tu)(dipy)Cl	1080	735
Ag(tu)(ophen)Cl	1080	730
Ntu	1085	725
Ag(Ntu)Cl	1095	770
Ag(Ntu)(py)Cl	absent	763
Ag(Ntu)(dipy)Cl	absent	765
Ag(Ntu)(ophen)Cl	absent	769
Dtu	1070	760
Ag(Dtu)Cl	1065	750
Ag(Dtu)(dipy)Cl	absent	757
Ag(Dtu)(ophen)Cl	absent	729

†Present address Department of Metallurgy & Material Science, University of Liverpool, Liverpool, England

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Chemistry Department F R RAHMANI
Aligarh Muslim University A U MALIK†
Aligarh, U P N AHMAD
India

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Oxovanadium(IV) complexes of some *ortho*-hydroxy ketoximes

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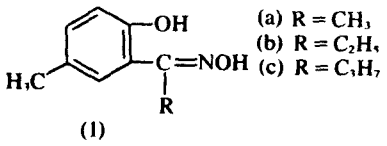
THE present work describes oxovanadium(IV) complexes of some salicylaldoxime based ligands

ortho-hydroxy 5 methylacetophenoneoxime—HMAO (1a)

ortho-hydroxy-5 methyl propiophenoneoxime—HMPO (1b)

and

ortho hydroxy-5-methyl butyrophenoneoxime—HMBO (1c)



(a) R = CH_3
(b) R = C_2H_5
(c) R = C_3H_7

(I)

Oxovanadium(IV) complexes with a variety of ligands have been extensively studied[1] But there are no reports on complexes of salicylaldoxime based ligands

EXPERIMENTAL

(a) *Preparation of complexes*

Ethanolic solution of the ligand and an aqueous solution of vanadyl sulphate were mixed together in a ratio of 2 1 Sodium hydroxide solution was added to raise the pH at pH 3 0 the complexes separated out The contents were digested on a water bath for about 1 hr The complexes were filtered washed successively with water and 50% ethanol solution and dried in an electric oven at ~80°C The complexes are insoluble in water and alcohol and soluble in other common organic solvents Results of elemental analyses and physical properties of the complexes are given in Table 1

(b) *Physical measurements*

Magnetic susceptibility measurements on the solid complexes were made at room temperature by the Gouy method using mercury tetrathiocyanato cobaltate(II) as a calibrating agent (χ_g = 16 44 × 10^{-6} cgs units) The visible absorption spectra (350–750 nm) of the complexes were recorded in chloroform on a Perkin-Elmer 37 UV visible spectrophotometer using a quartz cell Electron spin resonance spectra of powdered solid samples and also their chloroform solutions were recorded on a varian V 4502-12, EPR spectrometer having a 9 inch electromagnet (V3400) electrically fed with a highly stabilized and electrically regulated power supply (V-FR 2503) and a multipurpose mic rowave cavity (Type V-4531) The IR spectra of the complexes were recorded in KBr pellets on a Perkin Elmer infracord spectrophotometer

RESULTS AND DISCUSSION

The results of the magnetic susceptibility measurements are given in Table 2 Magnetic moments of the complexes lie in the range 1 66–1 69 B M, very near the spin only value for one unpaired spin, confirming the quadrivalent state of the central

Table 1 Elemental analyses

Compound†	m p (°C)	% C Found	% C Reqd	% H Found	% H Reqd	% N Found	% N Reqd
$VO(HMAO)_2$	201	56 0	54 7	5 60	5 57	6 87	7 09
$VO(HMPO)_2$	172	55 9	56 7	6 11	6 00	7 00	6 60
$VO(HMBO)_2$	170	58 9	58 5	6 63	6 65	6 28	6 20

†The abbreviations for the ligands here denote deprotonated ligands

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Short communication

STEPWISE FORMATION AND BINDING OF INDIUM TRICHLORIDE WITH SOME AMINO ACIDS IN AQUEOUS PHASE

BADRUDDIN KHAN, OMAR FAROOQ and NASEER AHMAD

Inorganic Research Laboratory, Chemistry Department, Aligarh Muslim University, Aligarh, U.P. (India)

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Introduction

Amino acids play a vital role in various biological systems and their metal complexes have been extensively studied due to the coordinating ability of amino and carboxylic groups [1—3]. In recent years a detailed study was made by the authors on the interaction of transition metals having unusual oxidation states and metals belonging to the platinum group [4—13]. From the present literature it appears that no effort has yet been made to calculate the stepwise equilibrium and overall stability constants of indium trichloride amino acid systems employing Bjerrum's [14] method modified by Albert [15] in aqueous medium. The present communication reports the stability and binding of In(III) with some amino acids. The relation $\Delta G^0 = -RT \ln K_s$ was employed to calculate the values of ΔG^0 at 24°C, where K_s = the overall stability constant of a particular system. All titrations were carried out in anaerobic condition.

Experimental

Amino acids such as glycine, DL-α-alanine, L-asparagine, DL-serine, DL-valine, L-proline, taurine (B.D.H., England, biologically pure products) and DL-phenylalanine, β-alanine, DL-methionine, L-leucine and DL-leucine (E. Merck, Germany), chromatographically pure, were used in these investigations and their aqueous solutions were prepared in doubly distilled air-free water. Indium trichloride (Schuchardt, Germany) was estimated gravimetrically [16]. pH-metric titrations were performed with an Elico-pH meter, model L-1 (India) in conjunction with glass and saturated calomel electrodes.

Results and discussion

For each system, pH-metric titrations in triplicate were performed in the order (a) 0.01 *M* amino acids, (b) 0.0033 *M* indium trichloride and (c) a mixture of amino acid and metal salt having overall concentration of 0.01 *M* and

0.0033 *M*, respectively. The strength 0.1 *M* of carbonate-free KOH was checked before employing it as a titrant. An appreciable shift was observed indicating thereby, the stepwise association of the ligand, amino acid with metal. Metal ion-amino acid (ligand) systems may be explained by considering the stepwise formation of complex species of different composition in solution phase, MA. MA_2, MA_3 ... MA_n, where A stands for ligand and M for metal ion and *n* for number of amino acid (ligand) molecules bound by the metal ion. In general, at equilibrium the concentration of each species is related to that of each of the other complex species by a series of expressions.

$k_1 = [MA]/[M][A]$, $k_2 = [MA_2]/[M][A]$ and $k_n = [MA_n]/[MA_{n-1}][A]$

In case of a 2+ metal ion binding two ligand groups, the values may be written as

$k_1 = \{MA^+\}/\{M^{2+}\}\{A^-\}$, $k_2 = \{MA_2\}/\{MA^+\}\{A^-\}$

and

$K_s = [MA_2]/[M^{2+}][A^-]^2$

where k_1 and k_2 are the stepwise equilibrium or association constants, and K_s, the overall stability constant, is the sum of the logarithms of the equilibrium constants.

$\log K_s = \log k_1 + \log k_2$

Concentrations are used for simplicity and convenience. As the complex formation starts, H^+ ions are released, and the measurements of the concentration of these ions provide a useful way to determine the extent of complexation of metal with amino acid in solution phase.

The values of stepwise equilibrium constants may be given as

$k_1 = \bar{n}/(1 - \bar{n})[Sc]$, $k_2 = (\bar{n} - 1)/(2 - \bar{n})[Sc]$

Here $\bar{n}$ is the average number of molecules of complex forming agent attached to one atom of the metal, and [Sc] is the concentration of the coordinating species, and values may be calculated from the relation given below:

$\log[Sc] = (pH - pK_a) + \log\{[HSc^0] - [KOH]\}$

This relation holds good between pH 3 and 11 and $[HSc^0]$ stands for the initial concentration of the amino acid before the addition of the metal and [KOH] is the concentration of the alkali when a complex forming agent (amino acid) and metal are both absent. $\bar{n}$ is governed by the relation

$\bar{n} = 2\,[KOH]/[HSc^0]$

The regular values of $\log k_1$, $\log k_2$ and $\log K_s$ are given in Table 1. The ranges are $\log k_1$ ($\bar{n}$ = 1.00—0.80) and $\log k_2$ ($\bar{n}$ = 1.26—1.80) respectively in all the cases reported herein. The plots, $\bar{n}$ vs. log[Sc] (formation curves) are given in Fig. 1 for a few amino acid-$InCl_3$ systems.

TABLE 1

System	$\log k_1$	$\log k_2$	$\log K_s$	$-\Delta G^0$/kJ mol^{-1}
DL-α-Alanine-$InCl_3$ system	8.40	8.25	16.65	94.63
β-Alanine-$InCl_3$ system	8 30	8.22	16.52	93.94
L-Asparagine-$InCl_3$ system	7.17	7.21	14.38	81.83
Glycine-$InCl_3$ system	8.22	8.02	16.23	92.34
DL-Leucine-$InCl_3$ system	7.76	7.65	15.41	87.64
L-Leucine-$InCl_3$ system	8.26	7.48	15.74	89.51
DL-Methionine-$InCl_3$ system	7.75	7.42	15.17	86.29
DL-Phenylalanine-$InCl_3$ system	7.36	7.22	14.58	82.95
L-Proline-$InCl_3$ system	9.04	8.64	17.68	100.64
DL-Serine-$InCl_3$ system	7.53	7.05	14.58	82.90
DL-Taurine-$InCl_3$ system	7.44	7.13	14.57	88.55
DL-Valine-$InCl_3$ system	8.28	7.52	15.80	89.85

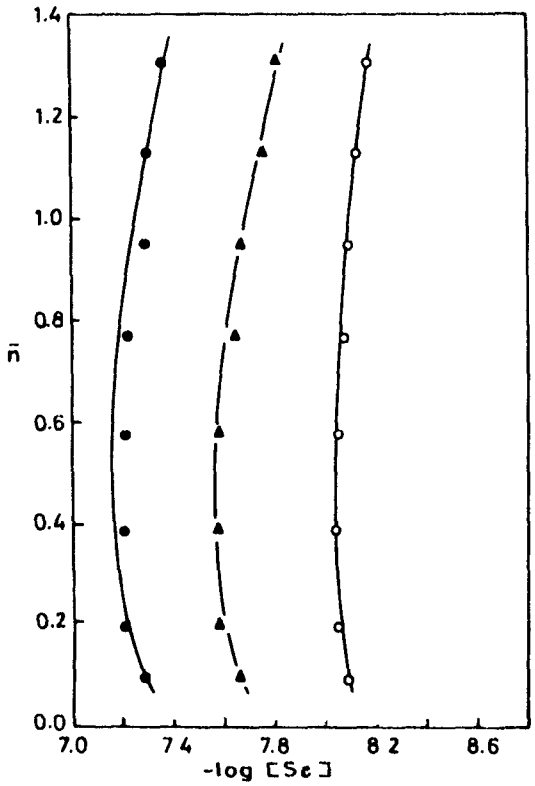

Fig. 1. Plots of n vs. log[Sc] for several amino acid-$InCl_3$ systems. (●) $InCl_3$-DL-phenylalanine system, (▲) $InCl_3$-DL-leucine system; (○) $InCl_3$-glycine system.

The stability constants of the systems vary from 17.68 (log K_s for L-proline) to 14.39 (log K_s for L-asparagine) and the order of the stability may be written as: L-proline > DL-α-alanine > β-alanine > glycine > DL-valine > L-leucine > DL-leucine > DL-methionine > phenylalanine > DL-serine > taurine > L-asparagine. Deviation is observed in a few cases perhaps due to the formation of polynuclear compounds [17]. In the majority of cases the values of $-2 \log[Sc]$ at $\bar{n} = 1$ correspond to the value of the log K_s.

The sulphur containing amino acids, methionine and taurine did not show any abnormality and appeared to behave like other simple amino acids. It may be said that thioether type sulphur in methionine, $CH_3SCH_2CH_2(NH_2)COOH$, contributes almost nothing to the stability of the complex [7—12]. In general, the value of log K_s decreases as the distance between the amino and carboxylic groups increases (between NH_2 and SO_2OH in the case of taurine [11]. The present study does not throw light on the part played by sulphur atom and the real mode of binding is only a matter of speculation.

The conductometric titrations revealed a ratio of 1 : 1 (metal : amino acid) in aqueous solution at 24°C. These observations could not be substantiated by other data due to the fact that the complexes could not be isolated in the solid state.

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MIXED LIGAND COMPLEXES OF DIPIVALOYLMETHANE AND PHTHALAZINE WITH RARE-EARTH METALS

M. S. ANSARI and N. AHMAD

(Department of Chemistry. Aligarh Muslim University, Aligarh, U.P India)

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M. S. ANSARI and N. AHMAD

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The mixed ligand complexes. tris(dipivaloylmethanato) phthalazinates of trivalent lanthanide (except Ce, Pm and Lu) were synthesized and characterized by elemental analyses, melting points, thermogravimetric analyses, magnetic moments, molar conductance and IR spectrum. The complexes are Ln(dpm).phth where Ln = trivalent lanthanide ion, dpm = dipivaloylmethane and phth-phthalazine. Thermogravimetric analysis shows that the dpm is removed first and phthalizine afterwards. The complex species volatilize at several stages so that the total weight loss is less than the weight loss calculated for the formation of the metal. The molar conductance values of the complexes are negligible signifying their non-electrolytic nature. The magnetic moments when plotted against the atomic numbers show the usual unequal double humped curve. The IR spectra is discussed.

Rare-earth β-diketonates have received considerable attention as pseudocontact n.m.r. shift reagents during recent years [1—6]. β-diketonates have also been used for the gas chromatographic separation of lanthanides [7—8]. A few attempts have been made to prepare mixed ligand complexes of rare-earths with some oxygen and nitrogen containing donors. CHARLES and OHLMANN [9] prepared 1 : 1 and 1 : 2 adducts of tris(dibenzoylmethane)europium (III) with a number of nitrogen and oxygen containing ligands. Mixed ligand complexes of rare-earths using β-diketones, 2,2'-dipyridyl and 1,10-phenanthroline have been reported [10—12]. SELBIN *et al.* [13] prepared rare-earth dipivaloylmethanate and their mixed adducts with pyridine, 2,2'-dipyridyl and 1,10-phenanthroline. They reported their m.p., thermograms, magnetic moments, Weiss constants, n.m.r. and electronic spectra.

In a previous communication [14], we reported the preparation of mixed ligand complexes of rare-earth dipivaloylmethane with pyrazine and characterized them by elemental analysis, m.p., thermogram, magnetic measurement, molar conductance and IR spectrum.

The present communication deals with the synthesis of the adducts of tris(dipivaloylmethane)lanthanides (except Ce, Pm and Lu) with phthalazine and their elemental analysis, m.p., thermogram, magnetic moment, molar conductance and IR spectrum.

Table I

Analyses and some characterizing data

Compounds	Colour	% C	% H	% N	M P °C	μ_{eff} (B M)	Molar cond $Ohm^{-1}cm^{2}mole^{-1}$
1. $La(dpm)_3Phth$	white	(60.32)	(7.72)	(3.421)	132°C	Diamag.	32.23
		61.01	7.85	3.52			
2. $Pr(dpm)_3Phth$	dirty white	(60.03)	(7.65)	(3.4)	133°C	3.59	26.89
		60.11	7.78	3.49			
3. $Nd(dmp)_3Phth$	violet	(59.78)	(7.65)	(3.39)	125°—28°C	3.61	27.64
		58.90	7.73	3.42			
4. $Sm(dpm)_3Phth$	white	(59.349)	(7.59)	(3.37)	125°C	1.85	22.41
		60.82	7.46	3.44			
5. $Eu(dpm)_3Phth$	white	(59.209)	(7.577)	(3.367)	200°C	3.76	22.41
		60.33	7.69	3.48			
6. $Gd(dpm)_3Phth$	white	(59.09)	(7.53)	(3.346)	115—18°C	8.11	22.41
		60.51	7.58	3.31			
7. $Tb(dpm)_3Phth$	white	(58.74)	(7.515)	(3.22)	112—15°C	9.87	17.67
		59.84	7.40	3.37			
8. $Dy(dpm)_3Phth$	white	(58.49)	(7.482)	(3.325)	120°C	10.3	14.11
		57.12	7.61	3.35			
9. $Ho(dpm)_3Phth$	light yellow	(58.32)	(7.46)	(3.316)	125°C	10.73	13.87
		59.32	7.58	3.46			
10. $Er(dpm)_3Phth$	pink	(57.336)	(7.44)	(3.307)	116—20°C	9.58	13.87
		58.43	7.52	3.41			
11. $Tm(dpm)_3Phth$	white	(57.048)	(7.426)	(3.300)	110—15°C	7.59	13.87
		56.80	7.40	3.33			
12. $Yb(dpm)_3Phth$	white	(57.768)	(7.39)	(3.284)	120—24°C	4.68	11.45
		58.99	7.45	3.11			

dpm dipivaloylmethane, Phth phthalazine, Calculated values are given in parentheses

Experimental

Rare-earth chlorides (Leico-Chemicals, U.S.A.), 2,2,6,6-tetramethyl-3,5-heptanedione (dipivaloylmethane) (Penn. Chem. Research U.S.A.) and phthalazine (Koch-Light Laboratories, England) were used to prepare the complexes without further purification.

Tris(dipivaloylmethane)lanthanide(III) compounds were prepared by the method of EISENTRAUT and SIEVERS [7] and BERG and ACOSTA [8]. The mixed ligand complexes with phthalazine were obtained by mixing the tris(dipivaloylmethane)lanthanide(III) complexes and phthalazine in 1 : 1 molar ratio in *n*-hexane.

The complexes were analyzed for carbon, hydrogen and nitrogen in the Microanalytical Section of this department. The melting points were determined with the usual method and the thermograms of five of these complexes were recorded between room temperatures and 800 °C.

The magnetic measurements were made at room temperature with the help of a Gouy balance. Diamagnetic corrections for the ligand were applied and the values of magnetic moments were plotted *versus* the atomic numbers of the rare-earths (Table I).

The molar conductances of $10^{-3}M$ solutions of the complexes were measured in methanol on a Philips PR-9500 conductivity bridge. The IR spectra of complexes were recorded in the range of 4000—600 cm^{-1} in KBr phase with a Perkin Elmer infra cord model 137B.

Results and discussion

The elemental analyses of the adducts obtained by the interaction of phthalazine with tris(dipivaloylmethane)-lanthanide(III) yielded the following formula:

$$M(dpm)_3phth$$

Where M stands for trivalent rare-earths, dpm for dipivaloylmethane and phth for phthalazine.

The complexes are quite stable and can be handled in air without any effect of air or moisture. They are insoluble in water but soluble in about all organic solvents. The molar conductances of these complexes at $10^{-3}M$ dilution in methanol are in the range of 11—32 Ohm^{-1} cm^2 $mole^{-1}$ which clearly proves their being non-electrolytes since the molar conductances of $10^{-3}M$ solutions of 1 : 1, 2 : 1 and 3 : 1 electrolytes are 80—115, 160—220 and 290—350 Ohm^{-1} cm^2 $mole^{-1}$ respectively. The complexes are thus inner complex non-electrolytes.

The magnetic moments of these complexes when plotted against the atomic numbers of the rare-earths show the usual unequal double humped curve (Fig. 1).

The thermogravimetric analysis curves for praseodymium, samarium, terbium, holmium and ytterbium show that the removal of first molecule of dipivaloylmethane is slow, that of the second is rapid and that of third is again quite rapid; the phthalazine is removed after the removal of dipivaloylmethane and the amount of metal left at the end is less than the amount expected on the basis of stoichiometric considerations as some complex species during combustion volatilizes leaving lesser amount for metal formation.

The IR spectrum of the tris(dipivaloylmethane) phthalazine lanthanides show shifting of all important bands to higher frequencies as compared to their

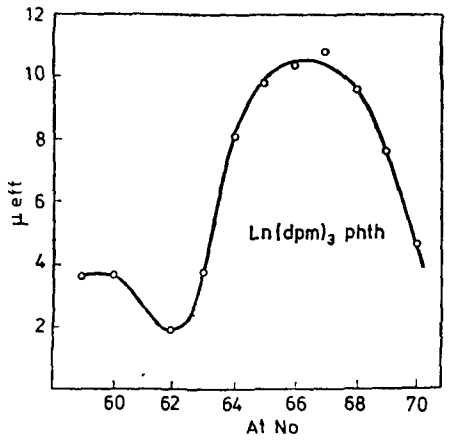

Fig. 1

positions in tris(dipivaloylmethane)lanthanides. For example in case of lanthanum the bands occurring at 3000, 1560, 1484, 1435, 1395, 1212, 1168, 1126 and 864 shift to 3049, 1583, 1508, 1453, 1404, 1179, 1138 and 686 cm^{-1}. The important peaks of phthalazine which appear at 765(vs), 917(s), 1211(m), 1245(m), 1277(m), 1305(m), 1374(m) and 1436(m) cm^{-1} in the ligand, completely disappear in the complex.

The phthalazine is thus coordinated to the lanthanide ions in tris(dipivaloylmethanates) raising their coordination number from six to seven.

*

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M. SHAMEEM ANSARI, Naseer AHMAD } Department of Chemistry, Aligarh Muslim University Aligarh, U. P. India.

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Notes

Schiff Base Complexes of Titanium(III)

S. F. H. Rizvi & Naseer Ahmad

Department of Chemistry, Aligarh Muslim University, Aligarh

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THE present day chemical literature records only a few Schiff base complexes of titanium(IV)[1,2] and had only one with titanium(III)[3]. We have recently reported eight new complexes of titanium (III) with Schiff bases[4]. The present communication deals with the synthesis, isolation and characterization—by elemental analyses, m.p.s, thermogravimetric analysis, molar conductance, infra red spectra and magnetic moments—of titanium(III) complexes with the Schiff bases of (a) 4-hydroxybenzaldehyde with ethylene diamine, *o*-phenylene diamine, dianisidine, benzidine, (b) 4-chlorobenzaldehyde with benzidine, dianisidine, *o*-phenylene diamine and (c) 2-methoxybenzaldehyde with *o*-phenylene diamine.

Experimental

Dianisidine, ethylene diamine, *o*-phenylene diamine and 2-methoxy benzaldehyde were reagent grade and used as such. $TiCl_3.6H_2O$ was synthesised[5], 4-chlorobenzaldehyde and 4-hydroxybenzaldehyde were recrytallised and 2-methoxybenzaldehyde was distilled before use.

The aldehyde and amine were taken in the molar ratio of 2 : 1 in ethanol, stirred for 2–4 hr and the resulting precipitate separated and washed with ethanol and recrystallised out. The purity of the ligands was ascertained by their elemental analysis for C, H and N.

The titanium(III) chloride was allowed to react with Schiff bases in the stoichiometric ratio of 1 : 1 with a slight excess of the Schiff bases in dry tetrahydrofuran. The precipitate was separated, washed with the same solvent and dried *in vacuo*. The whole of the work of synthesis was carried out in a dry inert glove bag because titanium(III) is susceptible to oxidation by air and prone to hydrolysis by moisture and the resulting complex is apt to decomposition and oxidation with air. The elemental analyses were done at this Department and at the Central Drug Research Institute, Lucknow. A known amount of the complex was fused with pure caustic potash in a platinum crucible, dissolved in dilute nitric acid and the chloride estimated as silver chloride.

Conductance was measured in DMSO with a Philips conductivity bridge model PR-9500 in conjunction with a dip type cell. The magnetic moments were determined by Gouy method and the diamagnetic correction for the ligands was applied. Thermograms were taken at the BARC, Bombay with a Bausch and Lomb thermogravimetric balance, at a heating rate of 6° per minute between room temperature and 520° in an inert atmosphere. The i.r. spectra of the complexes and the ligands were taken in KBr phase on a Perkin Elmer infra red spectrophotometer model 621.

Results and Discussion

Chemical analyses give the formulae for the complexes as given in the Table. Some of the hydrogen analyses are quite high because the complexes readily absorb moisture when exposed to air during micro-analyses.

The magnetic moment of these complexes after applying diamagnetic correction for the ligands lie in the range of 1.44 to 1.75 B.M., showing that the metal is in the trivalent state. The values lower than 1.73 B.M. might be due to the slight oxidation of the complexes. The same has been observed in the titanium(III) *o*-phenanthroline complex[6].

The molar conductances of these complexes are between 25.2 and 70.6 mhos per mole cm^2 in dimethylsulphoxide. This range is quite compatible with 1 : 1 electrolytes[7–8]. It suggests that, in all these complexes, one out of three chlorides is outside the coordination sphere and the remaining two are coordinated to the metal.

The high temperatures (see Table) at which the two water molecules in the complexes of bis(4-hydroxybenzaldehyde)dianisidine, bis(4-hydroxybenzaldehyde) benzidine and bis(4-chlorobenzaldehyde)dianisidine are eliminated as shown by TGA, proves that the two water molecules in these complexes are inside the coordination sphere. The tetrahydrofuran molecule present in bis(4-chlorobenzaldehyde)benzidine and bis(2-methoxybenzaldehyde) *o*-phenylene diamine complexes is removed respectively, at 228° and 230°, which prove that it is coordinated with the metal ion.

In i.r. the most important absorption is that of the CN stretching. Biradar and Kulkarni[9] reported that CN stretching occurs at 1625–30 cm^{-1} and is shifted to higher frquency, i.e. 1630–1650 cm^{-1} on complexation. This absorption occurs at 1635(s), 1619(s), 1650(s), 1620(s), 1625(s), 1620(m), 1602(s)

TABLE—ELEMENTAL ANALYSES AND OTHER CHARACTERISING DATA.

Complex	Elemental Analyses%				Colour	Magnetic moment	Λ_M Ohm^{-1} cm^2	Removal of water or tetrahydrofuran (% loss at temperature)		
	C	H	N	Cl		B.M.	mole^{-1}	1H_2O	2H_2O	1 THF
1	2	3	4	5	6	7	8	9	10	11
1. [($C_{16}H_{16}N_2O_2$)Cl_2Ti]Cl [Cl_2.bis(4-OH Benz)en Ti(III)]Cl	(41.90) 42.22	(6.16) 5.99	(6.63) 5.98	(18.65) 18.91	yellow	1.75	*	—	—	—
2. [($C_{20}H_{16}N_2O_2$)Cl_2Ti]Cl [Cl_2.bis(4-OH Benz) *o*-phen Ti(III)]Cl	(51.46) 51.14	(3.40) 3.44	(5.95) 5.86	(34.93) 33.90	dirty white	1.44	68.8	—	—	—
3. [($C_{26}H_{28}N_2O_5$)Cl_2Ti]Cl H_2O [Cl_2.2H_2O.bis(4-OH Benz)dian. Ti(III)]Cl.H_2O	(53.40) 53.52	(5.30) 5.53	(4.23) 4.39	(26.74) 26.56	yellow	*	22.7	68°C (2.54) 2.35	128°C (8.61) 8.51	—
4. [($C_{26}H_{24}N_2O_3$)Cl_2Ti]Cl [Cl_2.2H_2O.bis(4-OH Benz)Bn. Ti(III)]Cl	(48.45) 47.92	(4.78) 5.21	(4.82) 4.91	(16.10) 16.21	light yellow	1.48	29.7	—	180°C (5.99) 5.28	—
5. [($C_{30}H_{26}N_2OCl_4$)Ti]Cl [Cl_2.bis(4-Cl.Benz)Bn.THF. Ti(III)]Cl	(55.43) 55.08	(3.56) 4.63	(4.52) 4.58	(28.59) 27.40	dirty white	*	70.3	—	—	228°C (14.90) 14.30
6. [($C_{26}H_{26}N_2O_3$.Cl_4)Ti]Cl [Cl_2.2H_2O.bis(4-Cl Benz)dian. Ti(III)]Cl	(48.01) 48.03	(3.83) 4.01	(4.11) 4.08	(26.81) 26.04	brown	1.52	68.8	—	150°C (5.88) 6.00	—
7. [($C_{20}H_{14}N_2Cl_4$)Ti]Cl [Cl_2bis(4-Cl-Benz)*o*-phen Ti(III)]Cl	(49.41) 50.02	(3.16) 3.86	(5.52) 5.49	(25.12) 24.90	dirty white	1.47	69.9	—	—	—
[($C_{28}H_{28}N_2O_3Cl_2$)Ti]Cl [Cl_2bis(2-MeO Benz)*o*-phen. THF Ti(III)]Cl	(54.70) 54.68	(4.91) 4.39	(4.90) 4.91	(18.26) 17.90	dirty white	1.44	25.2	—	—	230°C (13.46) 13.40

* amount insufficient
Theoretical percentages are given in parentheses
THF = tetrahydrofuran; en = ethylene diamine; *o*-phen = orthophenylene diamine; dian = dianisidine; Benz = benzaldehyde; Bn = benzidine; MeO = methoxy.

and 1626(s) in these ligands and is in most cases shifted to higher frequency on complexation, i.e., 1651(s), 1650(s), 1645(s), 1650(s), 1650(m), 1620(s), 1639(s) and 1645(s) cm^{-1} respectively in the complexes arranged in the Table. In the complexes containing phenolic OH group there is no change in the i.r. spectra of the complexes in the region of OH formation, that is 1200 cm^{-1}, and 1410–1310 cm^{-1}. Hence it is concluded that coordination occurs through nitrogen and not through phenolic hydroxyl groups.

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Thermodynamic Ionization Constant of Salicyloylhydrazide in Aqueous Solution

R. K. BHATNAGAR, U. S. GUPTA & K. K. PANDE*

Chemical Laboratories, Government Science College, Gwalior

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MEASUREMENTS of the extent of ionization were previously made by the method of visual colorimetry by Hammett and coworkers[1] and also

* Head, Chemistry Department, Govt. Science College, Gwalior

Results and discussion

Bis-vanillin-*o*-phenylene diamine interacts with trivalent yttrium and lanthanide ions in the molar ratio of 1:1 giving products having the composition:

$$[C_{22}H_{18}N_2O_4M]\,Cl \cdot 3H_2O$$

Table I

Elemental analyses and some other data

Compounds	% C	% H	% N	% Cl	M. P. °C	Λ M ohm^{-1} cm^2 mole^{-1}
1. $LaLCl \cdot 3H_2O$	(43.85) 44.19	(3.983) 4.18	(4.647) 4.53	(5.883) 5.99	215—18°	69.1
2. $CeLCl \cdot 3H_2O$	(43.763) 45.21	(3.975) 4.03	(4.637) 4.72	(5.87) 5.76	218°	60.6
3. $PrLCl \cdot 3H_2O$	(43.70) 44.89	(3.975) 4.11	(4.631) 4.80	(5.864) 5.98	225—27°	49.8
4. $NdLCl \cdot 3H_2O$	(43.466) 44.0	(3.948) 4.13	(4.606) 4.80	(5.83) 5.90	225°	36.9
5. $SmLCl \cdot 3H_2O$	(43.034) 43.94	(3.908) 4.25	(4.560) 4.70	(5.773) 5.88	226.28°	40.5
6. $EuLCl \cdot 3H_2O$	(42.926) 44.11	(3.89) 4.13	(4.548) 4.66	(5.758) 5.90	178°	59.3
7. $GdLCl \cdot 3H_2O$	(42.555) 43.7	(3.883) 4.00	(4.509) 4.71	(5.709) 5.82	270°	65.4
8. $TbLCl \cdot 3H_2O$	(42.441) 43.92	(3.871) 4.09	(4.497) 4.50	(5.694)	168—70°	63.9
9. $DyLCl \cdot 3H_2O$	(42.198) 40.81	(3.833) 4.13	(4.471) 4.61	(5.66)	220—25°	46.3
10. $HoLCl \cdot 3H_2O$	(42.035) 41.95	(3.818) 4.11	(4.554) 4.38	(5.639) 5.80	215—20°	36.7
11. $ErLCl \cdot 3H_2O$	(41.878) 40.93	(3.804) 4.10	(4.438) 4.61	(5.619)	226—30°	27.5
12. $TmLCl \cdot 3H_2O$	(41.763) 43.25	(3.794) 4.02	(4.426) 4.33	(5.604)	230°	29.7
13. $YbLCl \cdot 3H_2O$	(40.557) 40.77	(3.769) 4.13	(4.303) 4.20	(5.568) 5.70	225—30°	29.6
14. $YLCl \cdot 3H_2O$	(47.639) 48.15	(4.325) 4.55	(5.067) 5.20	(6.414) 6.59	230—35°	40.1

L = Bis-vanillin benzidine calculated values are given in parentheses

Where M stands for lanthanide elements (except promethium and lutecium) and yttrium. according to elemental analyses for carbon. hydrogen. nitrogen and chlorine. The formation of these complexes involves the ionization of the two phenolic hydroxyl groups.

The molar conductances of these complexes at $10^{-3}M$ concentration in dimethyl sulphoxide are in the range of 27.5—69.1 ohm^{-1} cm^2 mole^{-1}. GREENWOOD [5] *et al.* reported 50—70 ohm^{-1} cm^2 mole^{-1} as the range for 1 : 1 electrolytes in this solvent and BROOMHEAD and KUNE-MAGUIRE [6] reported 24 and 27 ohm^{-1} cm^2 mole^{-1} molar conductances for ethylene diamine complexes of cobalt (III) and ruthenium (III) under the same conditions. It can be concluded that these complexes are 1 : 1 electrolytes and the chloride is in the outer co-ordination sphere.

Table II

Thermogravimetric analyses data

Compounds	Removal of one water molecule, % wt loss			Removal of three water molecule, % wt loss			Metal formation, % wt loss		
	Theo	Obs.	Temp °C	Theo	Obs.	Temp °C	Theo	Obs.	Temp. °C
1. $LaLCl \cdot 3H_2O$	2.987	3.0	100°	8.96	9.0	160°	76.95	80.0	550°
2. $PrLCl \cdot 3H_2O$	2.983	3.1	98°	8.949	9.0	168°	76.71	79.5	560°
3. $Sm \cdot Cl \cdot 3H_2O$	2.931	2.5	96°	8.793	8.5	150°	75.52	77.5	568°
4. $TbLCl \cdot 3H_2O$	2.892	2.5	110°	8.676	8.4	155°	74.48	78°	560°
5. $HoLCl \cdot 3H_2O$	2.86	3.0	108°	8.59	8.5	156°	73.77	79.5	566
6. YbLCl $3H_2O$	2.824	2.5	108°	8.472	8.4	150°	72.82	80.5	554°

The thermograms yield useful information. One water molecule is eliminated between 96° and 100 °C and all the three water molecules are lost up to 150—168 °C (Table II). The three water molecules seem to be co-ordinated to the lanthanide ions. The total weight loss observed is greater by 2.5—7% than the loss calculated for the removal of the ligand. water molecules and the chloride. Perhaps because the complex species volatilizes at various stages leaving less metal than required on the basis of stoichiometric considerations.

The infrared spectrum of bis-vanillin-*o*-phenylene diamine shows a medium intensity band at 3448 cm^{-1} which is also present in its complexes in the region of 3448—3534 cm^{-1} and is assigned to antisymmetric OH stretching mode. The IR spectra of complexes do not show any band near 1630 cm^{-1} which may be assigned to lattice water.

In bis-vanillin-*o*-phenylene diamine a medium intensity band appears at 1585 cm^{-1} which is the stretching frequency of the C = N bond. A strong band at 1428 cm^{-1} is the C-O stretching frequency of the phenolic part of vanillin. HENRY and DEHN [7] have reported the IR spectra of Schiff bases

and suggested that C = N absorption occurs at 1630 cm.$^{-1}$ GOLDBERG and NACE [8] have assigned very strong bands at 1630 and 1661 cm^{-1} for C = N stretching absorption. ROSE *et al.* [9] have reported C = N stretching frequencies at 1650(s) and 1660(s) cm.$^{-1}$ ROBSON *et al.* [10] assigned a broad band at 1610 cm^{-1} to imine C = N stretching frequency. BIRADAR and KULKARNI [11] have assigned the strong band at 1620—1610 to C = N stretching in Schiff base and found that this is shifted to higher frequency, 1650—1630 cm^{-1}, on complexation with titanium (IV). In our studies on lanthanide complexes of bis vanillin benzidine [12] it was observed that the two strong bands 1626 cm^{-1} (C = N stretching) and 1425 cm^{-1} (C — O stretching) shift to higher frequencies on complexation. In similar studies [4] on the complexes of bis-salicylaldehyde-*o*-dianisidine we observed that the 1613 cm^{-1} band shifted to higher frequency (1654—1629 cm^{-1}). The 1585 cm^{-1} and (CN stretching) and 1428 cm^{-1} band (C-O stretching) in bis-vanillin-*o*-phenylene diamine are shifted to higher frequency on complexation (1680—1613 and 1481—1494 cm^{-1} respectively).

The phenolic OH deformation occurring at 1389 cm^{-1} (medium) in the ligand disappears in the complexes.

A band appearing in the region of 865—873 cm^{-1} (strong) in the complexes is absent in the ligand and can be assigned to co-ordinated water.

On the basis of the shift of CN and C–O vibrations to higher frequencies, and the disappearance of the phenolic OH deformation, it is concluded that co-ordination occurs through both the phenolic oxygen atoms and the nitrogen atoms. The three water molecules are also co-ordinated making the rare-earth ions hepta-co-ordinate.

*

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N. SHAMEEM ANSARI
MASEER AHMAD
Department of Chemistry, Aligarh Muslim University
Aligarh, U.P. India.

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BIS-VANILLIN *o*-PHENYLENE DIAMINE COMPLEXES OF RARE-EARTHS

M. SHAMEEM ANSARI and NASEER AHMAD

(Department of Chemistry, Aligarh Muslim University, Aligarh, U. P. India)

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BIS-VANILLIN *o*-PHENYLENE DIAMINE COMPLEXES OF RARE-EARTHS

M. SHAMEEM ANSARI and NASEER AHMAD

(Department of Chemistry, Aligarh Muslim University, Aligarh, U. P. India)

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Bis-vanillin-*o*-phenylene diamine reacts with yttrium (III) and lanthanide (III) (except promethium and lutecium) ions to give 1:1 products having the composition $C_{22}H_{18}N_2O_4M\ Cl \cdot 3H_2O$. The molar conductance shows them to be 1:1 electrolytes and thermogravimetric analysis curves show that the three water molecules are co-ordinated. The infrared spectrum reveals the shifting of the C = N and C–O bands to higher frequencies on complexation. The co-ordination thus occurs through the two nitrogen atoms and both the oxygens of the phenolic OH groups making the rare earth ions heptaco-ordinate in these complexes.

A review of the present day chemical literature evinces the inadequacy of research on lanthanide (III) complexes of Schiff bases [1—2]. In previous papers [3—4] we have reported the lanthanide (III) and yttrium (III) complexes of tetradentate Schiff bases, bis vanillin-benzidine and bis salicylaldehyde-*o*-dianisidine.

The present communication deals with the synthesis of lanthanide (III) (except Pm and Lu) and yttrium (III) complexes of bis vanillin-*o*-phenylene diamine, which were characterized by their elemental and thermogravimetric analyses, melting points, molar conductances and infrared spectra.

Experimental

Rare-earth (III) chlorides (Leico Chemicals, U.S.A.) and yttrium (III) chloride (E. Merck, Germany) were used to prepare the complexes. The Schiff base bis-vanillin-*o*-phenylene diamine was prepared by the condensation of vanillin (Bush Boake Allen, London) and *o*-phenylene diamine in the molar ratio of 2:1 in ethanol, and purified by recrystallization from the same solvent.

The crystalline complexes were obtained by mixing the rare earth chlorides and the Schiff base in the stoichiometric ratio of 1:1 in ethanol and dried in vacuo.

The complexes were subjected to microanalysis for carbon, hydrogen and nitrogen, and chloride was estimated as silver chloride after fusing the complex with caustic soda in a platinum crucible.

The thermograms of six complexes (La, Pr, Sm, Tb, Ho and Yb) were taken at slow scan speed between ambient and 800 °C and the weight loss was plotted *versus* the temperature.

The molar conductances of $10^{-3}M$ solutions of these complexes in dimethyl sulphoxide were measured on a Philips PR 9500 conductivity bridge using a dip type cell.

The infrared spectra of the Schiff base and the complexes were recorded in the range of 4000—6000 cm^{-1} in KBr discs on a Perkin Elmer Infra Cord Model 137 B spectrophotometer.

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Cation Solvation: the Conversion of Contact Ion Pairs to Solvent Separated Ion Pairs

Sir:

Since the proposal by Winstein[1] of two types of ion pairs, many techniques have been developed to differentiate between them,[2] with the distribution depending on solvent donicity, cation size, anion, and temperature. It has also been found that in some systems two or more types of contact ion pairs can be observed,[3] whereas in other systems two or more types of solvent separated ion pairs can exist.[4] Focusing on the contact pairs, it is reasonable to imagine contact pairs with various extents of cation and/or anion solvation (solvated contact pairs). The question then arises as to how many solvent molecules are necessary to convert a contact ion pair to a solvent separated ion pair.

Attempts to answer this question have been complicated because of the nature of the usual electrolyte systems. In a pure solvent, the concentration of the solvating agent cannot be effectively varied, and one typically observes contact, solvent separated, or an equilibrium mixture of the two or more types of ion pairs.[2,5] But it is not possible to determine the extent of solvation of the ions. Mixed solvents could be used to overcome this problem.[2,6] However, they are generally unsatisfactory because of the solubility characteristics of the usual electrolytes, which result in the solvent and the selected donor competing for coordination sites on the ions.

The system sodium tetraethylaluminate ($NaAlEt_4$)-benzene-donor (D) is a particularly unique system for this type of study. $NaAlEt_4$ is soluble in benzene, a nonsolvating solvent. Thus controlled amounts of a solvating agent can be added to a benzene solution of $NaAlEt_4$, thereby permitting one to determine the ion pair type as a function of the D/Na^+ ratio. We wish to report here ratio studies using this system with a number of monodentate and bidentate solvating agents having Gutmann donor numbers ranging from 19.2 to 38.8.[7]

It is possible to distinguish between contact and solvent separated ion pairs in the $NaAlEt_4$-benzene-D system by examining the spin-spin interactions between ^{27}Al and ^1H as reflected in the methylene group proton resonance patterns.[8] In samples containing anions with cubic symmetry, the methylene absorptions appear as well-defined nine-line patterns representing the fortuitous overlapping of resonances resulting from essentially equal spin-spin interactions of methylene protons with both the neighboring methyl protons and the aluminum nucleus. Conversely, in samples containing highly distorted anions, the ^{27}Al-^1H spin interactions are not observed in the ^1H NMR spectra. Rather, the resonance collapses to a 1,3,3,1 quartet resulting from the remaining ^1H-^1H spin interactions. The two extremes, a nine-line pattern representing the anionic T_d symmetry and a quartet corresponding to the highly distorted anion are logically related to solvent separated and contact ion pairs, respectively.[9]

The preparation of $NaAlEt_4$, solvent, and sample preparation are described elsewhere.[10] The solvating agents were distilled over CaH_2 and handled as described earlier.[10] NMR spectra were obtained on Varian A-60A and HA100 spectrometers. Solutions of these systems tend to form two phases in benzene at certain ratios of donor/Na^+ with the salt and the solvating agent being predominantly in the lower phase. Some of the spectra shown are of the lower phase. Consequently, the concentrations of the salt and the solvating agent will show considerable variation, but since both remain in the lower phase, the D/Na^+ ratio is as listed. Except for a possible effect due to viscosity, the spectra are, in general, independent of this behavior. In those instances where a single phase is formed, the salt concentration is 0.26 M.

In Figure 1, a comparison of the methylene resonances is shown for $NaAlEt_4$ in benzene using diethyl ether (Et_2O), teterahydrofuran (THF), and hexamethylphosphoramide (HMPA) as solvating agents. For the 1:1 ratios of D/Na^+, the expected quartet characteristic of contact ion pairs is observed. However, using HMPA as the donor, a 4:1 ratio of HMPA/Na^+ gives a ^1H NMR spectrum characteristic of solvent separated ion pairs. In contrast, a 4:1 ratio of THF/Na^+ gives a ^1H NMR spectrum indicative of a preponderance of contact ion pairs. Finally, if we consider the limit where the donor is used as the solvent, it is seen that the methylene resonance in HMPA is essentially the same as it is for the 4:1 ratio of D/Na^+. When THF is used as the solvent, the nine-line pattern characteristic of solvent separated ion pairs is also observed. However, the resolution is poorer than that observed with

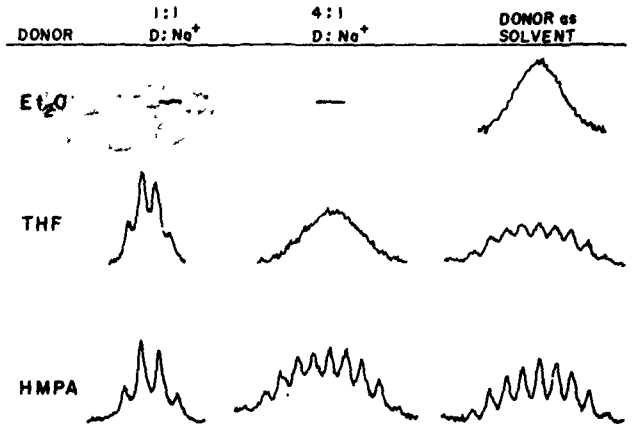

Figure 1. Methylene group resonance patterns in $AlEt_4^-$ for different ratios of donor/Na^+.

Table I. Donor/Na^+ Ratio to Give Solvent Separated Ion Pairs

Donor	D/Na^+ to give $[M^+//X^-]^0$	DN
Ethylenediamine (en)	2:1	
Dimethoxyethane (DME)	3:1–4:1	
Hexamethylphosphoramide (HMPA)	4:1	38.8
Dimethylformamide (DMF)	4:1–5:1 (probably 4:1)	30.9
Dimethyl sulfoxide (Me_2SO)	4:1–5:1	29.8
Pyridine (py)	>18:1	33.1
Tetrahydrofuran (THF)	>18:1	20.0
Diethyl ether (Et_2O)		19.2

HMPA. This has been attributed to an equilibrium between contact and solvent separated ion pairs,[9] but the distinctiveness of the nine-line pattern indicates a predominance of solvent separated ion pairs. On the other hand, when Et_2O is used as the solvent, the methylene resonance is indicative of a preponderance of contact ion pairs, thereby emphasizing the poor donor ability of Et_2O. Thus we see three cases; HMPA is a strong donor giving solvent separated ion pairs at a 4:1 ratio of D/Na^+; THF is an intermediate donor giving solvent separated ion pairs at high D/Na^+ ratios; and Et_2O is a sufficiently poor donor that it does not form solvent separated ion pairs with $NaAlEt_4$.

Analagous studies were made with a number of other donors, and the D/Na^+ ratios necessary to convert contact ion pairs to solvent separated ion pairs are given in Table I.

The observations for pyridine are particularly interesting. The Gutmann donor number for pyridine is 33.1, a very high value, and the correlation by Popov et al. of the ^{23}Na NMR chemical shifts with donor numbers substantiates this value.[11] More recently data has been obtained that brings the donicity of pyridine toward the Na^+ ion into question.[12] Although the results were logically rationalized in terms of solvent–solvent interactions, the observations reported here indicate that pyridine is, in fact, a rather poor donor toward the Na^+ ion. Based on the results of this study, a donicity toward the Na^+ ion similar in magnitude to that of THF would seem to be more reasonable. It is also interesting to note that DME is not as strong a donor as might be expected.

It is apparent from the above that for strong donors, a D/Na^+ ratio of 2:1 for bidentates and 4:1 for monodentates is sufficient to convert a contact ion pair to a solvent separated ion pair. But this is not to be construed to mean that the solvation number of the Na^+ ion is four. In previous studies, a solvation number of four has been proposed for the Na^+ ion,[13] but using Me_2SO as the donor, Wuepper and Popov reported a value of six.[14] Recent studies in this laboratory give support to the Wuepper and Popov value.[15]

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Naseer Ahmad, M. C. Day*
Chemistry Department, Louisiana State University
Baton Rouge, Louisiana 70803
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SCHIFF BASE COMPLEXES OF TITANIUM(III) AND VANADIUM(III)

S. FAKHRUL HASAN RIZVI and NASEER AHMAD

(Department of Chemistry, Aligarh Muslim University, Aligarh, India)

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S. FAKHRUL HASAN RIZVI and NASEER AHMAD

(Department of Chemistry, Aligarh Muslim University, Aligarh, India)

Received November 29, 1976

The complexes of titanium(III) with bis(2-methoxy benzalidene) dianisidine, bis(2-methoxybenzalidene) benzidine, bis(benzalidene) benzidine, bis(acetylacetone) benzidine, bis(acetyl acetone) ethylene diimine and bis(acetyl acetone) dianisidine and vanadium(III) with bis(benzalidene) *o*-phenylene diimine and bis(2-methoxy benzalidene) *o*-phenylene diimine have been synthesized and characterized by their elemental analyses, melting points, molar conductances, thermogravimetric analysis and infrared spectra. All the complexes show 1 : 1 ratio (Schiff base metal salt) and only one chloride is in the outer coordination sphere.

The preparation and characteristics of the complexes of titanium(IV) [1—3] and vanadium(IV) [4—6] with Schiff bases have been reported in the literature. However, the interaction of titanium(III) and vanadium(III) has been studied very vaguely. We have recently reported a number of titanium(III) complexes with Schiff bases [7]. The present communication deals with the complex formation between titanium(III) chloride and Schiff bases bis(2-methoxybenzalidene) dianisidine, bis(2-methoxy benzalidene) benzidine, bis(benzalidene) benzidine, bis(acetylacetone) benzidine, bis(acetylacetone) dianisidine, and bis(acetylacetone) ethylene-diimine and between vanadium(III) chloride and Schiff bases — bis(benzylidene)-*o*-phenylenediimine and bis(2-methoxybenzalidene)-*o*-phenylene-diimine. The complexes were isolated, subjected to elemental analysis for carbon, hydrogen, nitrogen and chlorine, their thermograms, molar conductances and infrared spectra taken and melting points determined.

Experimental

Benzidine (Reanal, Hungary), dianisidine (E. Merck, Germany), ethylenediamine (Riedel, Germany), *o*-phenylene-diamine (Xenon, Poland), benzaldehyde (Riedel, Germany), 2-methoxybenzaldehyde (Norda, U.S.A.), $TiCl_3 6H_2O$ [8], acetylacetone (B.D.H.) and vanadium(III) chloride (B.D.H., England) were used in these studies. 2-Methoxybenzaldehyde was distilled and benzidine, *o*-phenylenediamine were recrystallized before use.

The respective aldehydes and amines were taken in a mole ratio of 2 : 1 in benzene, stirred for about 3—4 hours and the resulting precipitate was washed with ethanol and recrystallized. The ligands were subjected to elemental analysis for carbon, hydrogen and nitrogen to establish their identity.

Preparation of the complexes

The complexes of Schiff bases with titanium(III) chloride and vanadium(III) chloride were prepared by reacting the metal and Schiff base in the mole ratio of 1 : 1 in dry tetrahydrofuran. The precipitate obtained was filtered in a Buchner base in dry tetrahydrofuran to remove any excess of the ligand. As titanium(III) and vanadium(III) chlorides are prone to oxidation and the complexes are highly hygroscopic, the whole process of preparation was done in an inert dry atmosphere. For this purpose a glove bag with constant flow of pure and dry nitrogen was improvized. After the washing of the complex was completed the precipitate was transferred quickly into a vacuum desiccator and dried. Since the complexes are insoluble in usual organic solvents, it was not possible to crystallize them. The complexes were analysed for carbon, hydrogen and nitrogen at the microanalytical section of this department. A given amount of the complex was fused with pure potassium carbonate in a platinum crucible, dissolved in dilute nitric acid solution and the chloride determined as silver chloride. The results are given in Table I.

Table I

Sl. No.	Complex	Carbon	Hydrogen	Nitrogen	Chloride	Colour	Solubility	λM Ohm^{-1} cm^{2}mole^{-1}
1.	Dichloro bis(2-methoxy--benz) dian Ti(III) Cl $[(C_{30}H_{28}N_2O_4Cl_2)Ti]$ Cl	56.76 (56.89)	4.45 (4.38)	4.41 (4.43)	16.75 (15.17)	Light brown	DMSO	27.4
2.	Dichloro bis(2-methoxy-benz) bn Ti(III) Cl -$[(C_{28}H_{24}N_2O_2Cl_2)$ Ti] Cl	58.51 (68.48)	4.21 (4.14)	4.87 (4.89)	18.50 (18.47)	Light yellow	DMSO	61.2
3.	Dichloro bis(benz) bn Ti(III) Cl $[(C_{26}H_{20}N_2Cl_2)$ Ti] Cl	60.67 (60.31)	3.92 (4.01)	5.44 (5.11)	20.66 (20.49)	Yellow	DMSO	58.3
4.	Dichloro bis(acac) bn Ti(III) Cl $[(C_{22}H_{24}N_2O_2Cl_2)$ Ti] Cl	52.56 (52.54)	4.81 (4.79)	5.57 (5.54)	21.45 (21.15)	Yellow	DMSO	71.1
5.	Dichloro bis(acac) dian Ti(III) Cl $[(C_{24}H_{28}N_2O_4Cl_2)]$ Ti Cl	51.22 (51.23)	5.02 (4.87)	4.98 (4.87)	18.90 (18.89)	Yellow	DMSO	70.9
6.	Dichloro bis(acac) en Ti(III) Cl $[(C_{12}H_{20}N_2O_2Cl_2$ Ti] Cl	38.07 (38.88)	5.33 (5.23)	7.40 (7.45)	28.10 (28.09)	Yellow	DMSO	70.8
7.	Dichloro bis(benz) *o*-phene-bis tetrahydrofuranato V(III) Cl $[(C_{20}H_{16}N_2Cl_2 \cdot 2\ C_4H_8O)$ V] Cl	57.40 (57.94)	5.51 (5.31)	4.78 (4.68)	—	Light pink	DMSO	52.3
8.	Dichloro bis(2-methoxy--benz) *o*-phene V(III) Cl dihydrate $[(C_{22}H_{20}N_2O_2\ Cl_2)$ V] 2 H_2O	49.14 (48.99)	4.50 (4.41)	5.21 (5.13)	—	Dirty white	DMSO	27.6

(The observed percentages for carbon, hydrogen, nitrogen and chlorine are given in parentheses)

Abbreviations used: en = ethylenediimine, dian = dianisidine, bn = benzidine, *o*-phene = *o*-phenylenediimine, benz = benzalidene, acac = acetylacetone.

Physico-chemical measurements

For the measurements of molar conductance, Philips conductivity bridge model PR9500 with a dip type conductivity cell was employed. Thermograms were taken at the Regional Research Laboratory, Hyderabad, India, for the complexes containing water, between room temperature and 500 °C in an inert atmosphere.

The i.r. spectra of the complexes and the ligands were taken in KBr phase between 4000 cm^{-1} and 700 cm^{-1}.

Results and discussion

Elemental analysis of carbon, hydrogen, nitrogen and chlorine give formulas for the titanium(III) and vanadium(III) Schiff base complexes (given in Table I) where the mole ratio between metal and the Schiff base is 1 : 1. Some of the hydrogen analyses are quite high because the complexes readily absorb moisture when exposed to air during microanalysis.

Since the complexes are very much susceptible to oxidation from atmospheric oxygen and prone to absorb moisture very readily and also because very small amounts of the samples were available, it was not possible to measure their magnetic susceptibility by the Gouy method.

The molar conductances of the complexes of titanium at 10^{-3} *M* concentration lie in the range of 27.4—71.1 $ohm^{-1} cm^2 mole^{-1}$, in dimethyl sulphoxide and for the complexes of vanadium(III) lie between 27.6 and 52.3 $ohm^{-1} cm^2 mole^{-1}$, which are compatible with 1 : 1 electrolytes [9]. It is therefore concluded that two of the three chlorides present are inside the coordination sphere leaving one outside.

The two complexes of vanadium(III) chloride with bis(benzylidene) *o*-phenylenediimine and bis(2-methoxybenzylidene) *o*-phenylenediimine which had indications of the presence of tetrahydrofuran or water were subjected to thermogravimetric analyses. The bis(benz) *o*-phenylenediimine complex shows the removal of the two tetrahydrofuran molecules at 225 °C (observed weight loss = 26%, theoretical for two tetrahydrofuran molecules = 25.03%). The total weight loss is 93% at about 460 °C. The bis(2-methoxybenzylidene) *o*-phenylenediimine complex shows that the removal of two water molecules is completed at only 50 °C (observed weight loss is 5.6%, theoretical 6.38%). The total observed weight loss is 99.5% at 425 °C. Since the total weight losses are 93% and 99.5% it is possible that during heating complex species is formed which volatilizes leaving little residue in the thermogravimetric balance. The two tetrahydrofuran molecules in the bis(benz) *o*-phene complex must be coordinated and the two water molecules in the vanadium(III) chloride complex of bis(2-methoxybenz) *o*-phene are present as lattice water.

The i.r. spectra of titanium(III) complexes in the region of 4000—2800 cm^{-1} in general contain bands in metal chelates of bis(acetylacetone)-ethylenediimine and related compounds [10] for the hydrogen bonded C–H or N–H. The hydrogen bonding between nitrogen and hydrogen is very weak and hence only in a few cases some bands have appeared in the region of 3700 and 3000 cm^{-1}. The bis(acetylacetone) benzidine, bis(acetylacetone) dianisidine and bis(acetylacetone) ethylenediimine show bands at 2950—3300 (b), 2980 (w) and 3450 (b) cm^{-1}, respectively. The titanium(III) complex with bis(acetylacetone) benzidine has a broad band at 2950 and that of bis(acetylacetone) ethylenediimine at 2750 whereas the complex of bis(acetylacetone) dianisidine

does not show any band in this region. These bands may be due to weak hydrogen bonding.

In the region of 1700 – 800 cm^{-1} the most important absorption is that of the C=N stretching. BIRADAR and KULKARNI [11] have reported that the C=N stretching vibration occurs at 1625 – 1630 cm^{-1} and is shifted to higher frequencies, *i.e.* 1630 – 1650 on complexation. This absorption occurs at 1605 (s). 1630 (s), 1613 (s), 1610 (s), 1606 and 1603 (s) in the ligands and is shifted to higher frequencies on complexation, that is to 1640 (vs), 1635 (m), 1618 (s). 1615 (s). 1618 (s) and 1632 (s), respectively, in the order given in Table I. The other bands in this region are due to phenyl ring and CH_3 and CH_2 deformation vibrations.

The complexes of Schiff bases, derived from acetylacetone and three amines, benzidine, dianisidine, and ethylenediamine show bands at 1365 (m). 1510 (s); 1355 (s) 1520 (m); 1380 (s) 1580 (m) which were present at 1345 (s). 1510 (m); 1325 (s), 1510 (s); 1350 (m) in their ligands, respectively. The bands show shifts to higher frequency thus signifying that coordination also occurs through the oxygen of the carbonyl groups of the Schiff bases derived from acetylacetone [12].

The most important feature of i.r. spectra of the complexes of vanadium(III) Schiff bases is the reduction in the number of bands of the ligands on complexation.

The bands of tetrahydrofuran do not appear in the IR spectra of dichloro bis(benzalidene) *o*-phenylenediimine bis tetrahydrofuranato vanadium(III) chloride. Tetrahydrofuran absorbs at 1076 cm^{-1}. Perhaps this band very much decreases in intensity and thus disappears as a result of coordination of tetrahydrofuran with the metal.

The complex bis(2-methoxybenzalidene) *o*-phenylenediimine vanadium(III) contains two water molecules. The i.r. spectra show a strong band at 1651 cm^{-1} and a broad band at 3280 – 3350 cm^{-1}, signifying the presence of lattice water [13].

The i.r. spectra of the complexes do not have any bands which may be assigned to V=O vibration. This is a clear proof of the fact that the complexes have been well protected from the atmospheric oxygen and are not oxidized.

The most important i.r. absorptions in the ligands occur at 1630 (s) and 1612 (s) cm^{-1} which shift to higher or lower frequencies on complexation. *i.e.* to 1605 (s), and 1630 (vs) in the complexes of vanadium(III) with bis-(benz)*o*-phene and bis(2-methoxy benz)*o*-phene, respectively. This is due to C=N stretching [10].

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S. Fakhrul Hasan RIZVI
Naseer AHMAD
Aligarh Muslim University
Aligarh 202001, U.P., India.

Table 1 Equilibrium data for reaction (3) at 28 (±0 5)°(μ = 0 6 M 10^4 [complex], M = 4 95(3-NO_2) 10^3[complex], M = 2 86 (*m*-OH) M = 2 97 (*p*-OH)

Complex [Fe(III)] $\times 10^3$	$[HClO_4]$ $\times 10^2$	D_{440}	$1/(\epsilon_1 - \epsilon_1)1$	$1/(\epsilon_2 - \epsilon_1)1$ K_M	K_M
3-Nitrosalicylato					
0 00	5 00	0 031			
2 00	5 00	0 175			
4 00	5 00	0 243			
8 00	5 00	0 384	7 59(±0 62) × 10 ^{4}	10 9(± 0.5) × 10 ^{5}	6 95(±0 65)
10 0	5 00	0 428			
15 0	5 00	0 484			
20 00	5 00	0 528			
10 0	10 0	0 290			
10 0	20 0	0 204			
m-hydroxybenzoato					
0 00	1 00	0 172			
1 70	1 03	0 178			
3 40	1 06	0 183			
6 80	1 12	0 192	2 37(±0 56) × 10 ^{2}	7 36(±0 19) × 10 ^{2}	3 22(±0 76) × 10 ^{1}
8 50	1 15	0 198			
13 0	1 20	0 202			
17 2	1 28	0 205			
p-Hydroxybenzoato					
0 00	1 00	0 190			
1 70	1 03	0 203			
3 40	1 06	0 210			
6 80	1 12	0 230	1.72(±0 73) × 10 ^{2}	3 64(±0 25) × 10^{-2}	4 73(±2 05) × 10 ^{1}
8 50	1 15	0 232			
13 0	1 20	0 255			
17 2	1 28	0 270			

cylato), like the free ligands, act as chelating agents towards the metal ions

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Department of Chemistry R K NANDA*
Utkal University A C DASH
Bhubaneswar-4 H K PATNAIK†
India

†Present address Department of Chemistry, B J B College, Bhubaneswar 6, India

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Studies on mixed ligand complexes of Ag(I)—II. Interaction of silver halides with substituted thiourea and heterocyclic amines

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The interaction of silver halide thiourea complexes with heterocyclic amines results in the formation of mixed ligand complexes[1–6] In this process Ag^+ achieves its highest coordination by forming 4-coordinate complexes

This paper reports the formation of 28 mixed ligand complexes of Ag(I) halides with nitrogen and sulphur containing ligands The ligands include substituted thioureas (allyl-, *o*-tolyl- and phenyl-) and heterocyclic amines (pyridine, 2,2'-dipyridyl and 1,10-phenanthroline) The mode of coordination has been discussed on the basis of the IR spectra of the complexes

EXPERIMENTAL

n-Allyl thiourea (Atu), *o*-tolyl thiourea (Ttu) and phenyl thiourea (Ptu) were B D H reagent grade and were purified by recrystallisation in acetone Pyridine (py) 2,2'-dipyridyl (dipy) and 1,10-phenanthroline (*o*-phen) were AnalaR products Freshly

Table 1 Chemical analyses and some characterising data

S No	Compounds	Metal (%)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	M pt °C	Colour	M_2 $\Omega^{-1}cm^2 mole^{-1}$
1	Mono(Atu) silver(I) chloride	40 85	17 98	3 59	10 38	190	White	4 3
	$C_4H_8AgClN_4S$	(41 56)	(18 49)	(3 08)	(10 78)			
2	Mono(Atu)mono(py)silver(I)chloride	32 24	31 84	3 68	12 82	132	White	16 1
	$C_4H_{13}AgClN_3S$	(31 85)	(31 89)	(3 83)	(12 40)			
3	Mono(Atu)mono(dipy)silver(I)	25 84	40 64	3 82	13 42	185	Purplish	10 0
	chloride	(25 94)	(40 41)	(3 84)	(13 46)		white	
	$C_{14}H_{16}AgClN_4S$							
4	Mono(Atu)mono(ophen)silver(I)	24 66	43 62	3 48	12 88	164	White	19 3
	chloride	(24 53)	(43 66)	(3 63)	(12 73)			
	$C_{16}H_{16}AgClN_4S$							
5	Mono(Atu)silver(I)bromide	35 64	15 02	2 35	9 14	182	White	5 2
	$C_4H_8AgBrN_2S$	(35 52)	(15 08)	(2 6)	(9 21)			
6	Mono(Atu)mono(py)silver(I)bromide	28 68	28 42	2 46	10 46	112	White	10 6
	$C_9H_{13}AgBrN_3S$	(28 16)	(28 19)	(3 96)	(10 96)			
7	Mono(Atu)mono(dipy)silver(I)	23 64	36 48	3 52	12 16	156	Purplish	6 3
	bromide	(23 44)	(36 50)	(3 47)	(12 17)		white	
	$C_{14}H_{16}AgBrN_4S$							
8	Mono(Atu)mono(ophen)silver(I)	22 26	39 88	3 25	11 54	198	White	8 4
	bromide	(22 27)	(39 65)	(3 30)	(11 56)			
	$C_{16}H_{16}AgBrN_4S$							
9	Bis(Ttu)silver(I)chloride	16 82	54 64	4 72	8 59	151	White	16 1
	$C_{30}H_{32}AgClN_4S_5$	(16 46)	(54 85)	(4 89)	(8 53)			
10	Bis(Ttu)mono(py)silver(I)chloride	14 68	57 54	5 12	9 64	132	White	6 4
	$C_{35}H_{37}AgClN_5S_5$	(14 67)	(57 12)	(5 03)	(9 52)			
11	Bis(Ttu)mono(ophen)silver(I)bromide	12 82	60 42	4 98	10 62	102	Yellowish	9 0
	$C_{47}H_{40}AgClN_6S_5$	(12 88)	(60 26)	(4 78)	(10 04)		white	
12	Bis(Ttu)silver(I)bromide	15 46	50 36	4 30	7 84	166	White	14 3
	$C_{30}H_{32}AgBrN_4S_5$	(15 39)	(51 38)	(4 56)	(7 84)			
14	Bis(Ttu)mono(dipy)silver(I)bromide	12 62	56 42	4 68	9 09	128	White	10 8
	$C_{40}H_{40}AgBrN_6S_5$	(12 59)	(56 02)	(4 66)	(9 80)			

15	Bis(Ttu)mono(ophen)silver(I)bromide $C_{42}H_{40}AgBrN_6S_3$	12 64 (12 24)	57 48 (57 22)	4 44 (4 54)	9 61 (9 53)	184	Light yellow	8 7
16	Mono(Ttu)silver(I)iodide $C_{15}H_{16}AgIN_2S$	22 46 (22 08)	36 83 (36 72)	3 10 (3 26)	5 22 (5 71)	188	White	6 1
17	Mono(Ttu)mono(dipy)silver(I)iodide $C_{25}H_{24}AgIN_4S$	16 87 (16 68)	46 22 (46 41)	3 39 (3 71)	8 58 (8 66)	218	Dirty white	4 6
18	Mono(Ttu)mono(ophen)silver(I)iodide $C_{27}N_{24}AgIN_4S$	16 24 (16 09)	48 64 (48 33)	3 52 (3 58)	8 98 (8 35)	242	Light yellow	8 4
19	Bis(Ptu)silver(I)chloride $C_{14}H_{16}AgClN_4S_2$	23 33 (23 77)	30 98 (30 7)	3 44 (3 52)	12 05 (12 34)	174	White	7 6
20	Bis(Ptu)mono(dipy)silver(I)chloride $C_{34}H_{32}AgClN_6S_2$	17 45 (17 70)	46 86 (47 21)	3 54 (3 93)	13 98 (13 77)	152	Pinkish white	4 3
21	Bis(Ptu)mono(ophen)silver(I)chloride $C_{36}H_{32}AgClN_6S_2$	16 92 (16 86)	49 42 (49 21)	3 88 (3 94)	13 34 (13 24)	125	Yellowish white	8 4
22	Bis(Ptu)silver(I)bromide $C_{14}H_{16}AgBrN_4S_2$	20 92 (21 68)	33 44 (33 72)	3 28 (3 21)	11 00 (11 24)	140	White	8 4
23	Bis(Ptu)mono(py)silver(I)bromide $C_{19}H_{21}AgBrN_4S$	18 76 (18 68)	36 11 (36 22)	3 51 (3 6)	12 02 (12 12)	128	Brown	16 1
24	Bis(Ptu)mono(dipy)silver(I)bromide $C_{34}H_{32}AgBrN_6S_2$	14 46 (14 28)	39 47 (38 17)	3 08 (3 18)	10 97 (11 13)	116	Pink	8 7
25	Bis(Ptu)mono(ophen)silver(I)bromide $C_{36}H_{32}AgBrN_6S_2$	26 45 (26 21)	45 56 (45 98)	3 58 (3 53)	12 35 (12 38)	165	White	16 8
26	Bis(Ptu)silver(I)iodide $C_{14}H_{16}AgIN_4S_2$	19 64 (19 78)	30 82 (30 81)	2 90 (2 93)	9 91 (9 9)	148	White	9 6
27	Bis(Ptu)mono(dipy)silver(I)iodide $C_{34}H_{32}AgIN_6S_2$	15 68 (15 37)	40 94 (41 05)	3 52 (3 42)	11 84 (11 97)	174	Pink	5 4
28	Bis(Ptu)mono(ophen)silver(I)iodide $C_{36}H_{32}AgIN_6S_2$	14 72 (14 86)	42 84 (43 00)	3 32 (3 30)	11 64 (11 50)	195	Yellow	7 6

Calculated values are given in parentheses Atu = allyl thiourea Ttu = *o* tolyl thiourea Ptu = phenyl thiourea pv = pyridine dipy = 2,2 dipyridyl ophen = 1 10 phenanthroline

Table 2 IR absorption bands of the complexes from 4000–600 cm $^{-1}$

Compounds	NH deformation	νN–C–N	ν(C–N	ν(C–S
1 Allyl thiourea	1620 m	1430 m	1060 s	620 m
2 Mono(Atu)silver(I)chloride	1620 m	1490 sh	—	760 m
3 Mono(Atu)mono(dipy)silver(I)chloride	1620 b	—	—	—
4 Mono(Atu)mono(ophen)silver(I)chloride	1620 m	1420 m	—	720 s
5 Mono(Atu)silver(I)bromide	1625 m	1500 s	—	790 s
6 Mono(Atu)mono(ophen)silver(I)bromide	—	—	—	715 m
7 Tolyl thiourea	1610 s	1490 m	1100 m	760 m
8 Bis(Ttu)silver(I)chloride	1520 w	1485 w	1100 m	745 s
9 Bis(Ttu)mono(py)silver(I)chloride	1520 m	1490 m	1100 n	750 m
10 Bis(Ttu)mono(ophen)silver(I)chloride	1540 m	1500 m	1105 m	750 s
11 Bis(Ttu)silver(I)bromide	1530 w	1490 w	—	745 s
12 Bis(Ttu)mono(dipy)silver(I)bromide	1530 w	1495 w	1110 m	750 s
13 Bis(Ttu)mono(ophen)silver(I)bromide	1600 m	1505 m	1110 b	740 s
14 Mono(Ttu)mono(dipy)silver(I)iodide	1530 b	1490 b	1110 m	730 m
15 Mono(Ttu)mono(dipy)silver(I)iodide	1530 b	1495 b	1110 m	755 s
16 Mono(Ttu)mono(ophen)silver(I)iodide	1590 w	1500 w	—	760 m
17 Phenyl thiourea	1605 m	1500 w	1055 m	740 vs
18 Bis(Ptu)silver(I)chloride	1610 b	1500 w	—	755 m
19 Bis(Ptu)mono(dipy)silver(I)chloride	1620 b	1500 m	1030 w	760 s
20 Bis(Ptu)mono(ophen)silver(I)chloride	—	—	—	760 m
21 Bis(Ptu)silver(I)bromide	10605 m	1510 w	1050 w	740 m
22 Bis(Ptu)mono(py)silver(I)bromide	1620 m	1500 m	—	745 m
23 Bis(Ptu)mono(dipy)silver(I)bromide	1600 m	1500 w	1060 w	735 s
24 Bis(Ptu)mono(ophen)silver(I)bromide	1600 m	1495 m	1060 w	750 m
25 Bis(Ptu)silver(I)iodide	1610 w	1520 w	1030 m	730 m
26 Bis(Ptu)mono(dipy)silver(I)iodide	1590 m	1505 s	1035 w	740 s
27 Bis(Ptu)mono(ophen)silver(I)iodide	—	1530 m	1030 w	770 s

prepared silver halides were used to prepare the complexes

Preparation of the complexes The complexes were synthesised by more or less the same procedure described earlier[7] Firstly the complexes of silver halides with substituted thioureas were prepared by adding the ligand solution to a suspension of silver halide (both in acetone) the mixture was vigorously shaken warmed and the undissolved silver halide was filtered off The complex was crystallised from the filtrate and dried *in vacuo* The preparation of the mixed ligand complex was accomplished by adding amine to the silver halide substituted thiourea complex in acetone The crystals of the mixed ligand complex appeared after 24–48 hr The complexes were microanalysed for C H and N For the estimation of silver the halide method was found to be unsatisfactory however, conversion of Ag into Ag_2O by heating a weighed amount of the complex gives satisfactory results

The molar conductances of the complexes (1.0×10^{-3} M in dimethyl sulphoxide) were obtained with a PR 9500 Philips Conductivity bridge and a dip type cell

The results of chemical analysis and molar conductance measurements are given in Table 1

The IR spectra of the complexes were taken in KBr medium in the range 600–4000 cm $^{-1}$ using a Beckman IR-spectrophotometer The characteristic peaks in the spectra are given in Table 2

RESULTS AND DISCUSSION

Complexes of the type $Ag(subs\ tu)_n$ (amine)X have been prepared and shown to be essentially non conducting in dimethyl sulphoxide[8] Where $n = 2$ the complexes are possibly 5 coordinate whereas where $n = 1$ 4 coordination is likely

On the basis of the IR spectra of complexes the mixed ligand complexes can be classified into two categories (1) complexes in which NH_2 bending and C–N stretches of the substituted thiourea shift to higher wave numbers whereas C–S stretches shift to the lower frequency side(II) complexes in which no significant shift in NH_2 bending modes is observed and C–N stretches disappear but there is an appreciable increase in C–S stretching frequency All the complexes show characteristic frequencies of the coordinated amine In the first category o tolyl thiourea complexes seem to coordinate through the sulphur and in the second category coordination through nitrogen cannot be excluded for allyl thiourea and phenyl thiourea mixed complexes

Inorganic Research Lab F R RAHMANI
Chemistry Department A U MALIK
Aligarh Muslim University N AHMAD
Aligarh U P
India

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THE SOLVATION NUMBER OF THE SODIUM ION

NASEER AHMAD and M. C. DAY*
Chemistry Department, Louisiana State University, Baton Rouge, LA 70803, U.S.A.

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Abstract—A new method for the determination of the inner sphere solvation number of the sodium ion is presented based on the distribution of donor between two liquid phases. The system sodium tetraethylaluminate ($NaAlEt_4$)–benzene (or cyclohexane)-donor forms two liquid phases with the salt in the lower phase and the distribution of donor between the two phases being strongly affected by solvation with the salt A solvation number of six is obtained with tetrahydrofuran, pyridine, dimethoxyethane and dimethylsulfoxide

INTRODUCTION

For many years there has been an interest in the solvation number of various cations and, because of its importance in biological systems, there has been a particular interest in the solvation number of the sodium ion. Solvation phenomena are complicated by the fact that a number of different species can exist in a given salt solution. If the solvent is restricted to water, both the cation and the anion will be hydrated; the extent depending on ion size, charge, and geometry and, for a small cation, there will be several solvation sheaths. On the other hand, in a nonaqueous solvent, quite different results may be expected. If the solvent dielectric constant is sufficiently low, the anion may occupy a site on the cation along with the solvent molecules forming a contact ion-pair. At higher concentrations, triple ions and higher aggregates might result. It also should be noted that most of the conventional nonaqueous solvents are Lewis bases and, therefore, tend to solvate with the cation to a much greater extent than with the anion. With salts having large anions, one can frequently assume only cation solvation is of importance.

Until quite recently the methods used to determine solvation numbers were not capable of distinguishing between these various effects, and it was generally found that the magnitude of the solvation number obtained depended on the experimental technique used. But with the development of spectroscopic methods, it would seem that these problems have been overcome and one should be able to directly determine the inner sphere solvation number of an alkali metal cation. For the sodium ion, the direct measurements are summarized in Table 1, where it can be seen that solvation numbers of both 4 and 6 have been proposed.

Along with the direct measurements, there has also been considerable indirect evidence for both a value of four[7–13] and a value of six[9, 14–18]. Additionally, ratio studies of the system $NaAlEt_4$-benzene-donor show that for strong donors, a donor:Na^+ ratio of four is sufficient to convert a contact ion-pair to a solvent separated ion-pair[19], again supporting a value of four for the inner sphere solvation number.

We wish to report here a new method for the determination of solvation numbers of alkali metal cations based on the distribution of the solvating agent (donor) between two liquid phases. The system $NaAlEt_4$–benzene (or cyclohexane)-donor forms two liquid phases at certain donor:Na^+ ratios with the salt occuring in the lower phase. The donor is distributed between the two phases, but its distribution is strongly affected by complexation with the cation. If the donor is a strong solvating agent, it would be expected to occur predominantly in the lower phase until the cation is solvated. After solvation, any additional donor would then be free and, therefore, distributed in both phases. A corresponding increase in donor concentration in the upper phase should be observed. For a weak solvating agent, the presence of donor in the upper phase will be

*Author for correspondence.

Table 1. Summary of direct solvation number determinations for the sodium ion

Method	Donor*	Salt**	Solvation Number	Reference
X-ray Diffraction	H_2O	$NaBF_4$	6	1
^{1}Hnmr	THF	$NaAlBu_4$	4	2
IR	THF	$NaAlBu_4$	4	3
^{1}Hnmr	MP	$NaAlBu_4$	4	4
^{1}Hnmr	DMSO	$NaAlBu_4$	6	4
Mass Spectrometry	H_2O	---	4	5
IR	PC	$NaB\phi_4$	6	6

* THF (tetrahydrofuran); MP (1-methyl-2-pyrrolidone); DMSO (dimethylsulfoxide); PC (propylene carbonate)

** $NaAlBu_4$ (sodium tetra-n-butylaluminate)

noted even at low donor:Na^+ ratios, but the distribution should, nevertheless, depend upon the solvation number of the cation. This dependence can be determined by monitoring the concentration of the donor in the upper phase.

EXPERIMENTAL

The preparation of $NaAlEt_4$ and the solvents is reported elsewhere[20]. The donors were all purchased as reagent or higher grade chemicals and were distilled over CaH_2 under a N_2 atmosphere.

All sample preparations were carried out in a N_2 atmosphere drybox. A circulating system passed the drybox atmosphere through a copper oven to remove oxygen, through 3A molecular sieves and a dry ice trap to remove moisture and organic vapors, and through a column of MnO as a final scavanger.

Samples were prepared by making up a series of flasks containing 0.25 g $NaAlEt_4$ in 5 ml benzene or cyclohexane (~0.3 M). The appropriate amount of donor was then added to each flask to give the desired donor:Na^+ ratio. This method results in a variation in the concentration between samples. Thus it is assumed that the solvation number is not concentration dependent over a moderate (~25%) concentration range.

The concentration of donor in the upper phase was determined by integration of selected donor ^1H NMR peaks relative to that of the solvent.

RESULTS AND DISCUSSION

In order for this technique to be applicable, it is necessary that the system salt-solvent-donor form two phases in the region of interest. We have studied a number of donors using $NaAlEt_4$ as the salt and both cyclohexane and benzene as the solvent with the D:Na^+ ratios ranging between 1:1 and 10:1. $NaAlEt_4$ is insoluble in both of these solvents at room temperature. Consequently, a minimum D:Na^+ ratio of 1:1 is necessary before solubility or two phasing is possible. As can be seen in Table 2, single phases, two phases, and

Table 2. Summary of two phase systems with $NaAlEt_4$-solvent-donor between D:Na^+ ratios of 1:1 and 10:1

	Solvent	
Donor	cyclohexane	benzene
	2 phases	1 phase
tetrahydrofuran	$D:Na^+ \geq 1:1$	$D:Na^+ \geq 1:1$
pyridine	2 phases	1 phase
	$D:Na^+ \geq 1:1$	$D:Na^+ \geq 1:1$
dimethylsulfoxide	insoluble	2 phases
	$D:Na^+ \leq 5:1$	$D:Na^+ \geq 1:1$
dimethoxyethane	insoluble	2 phases
	$D:Na^+ \leq 3:1$	$D:Na^+ \geq 1:1$
dimethylformamide	2 phases	2 phases
	$D:Na^+ \geq 1:1$	$D:Na^+ \leq 6:1$

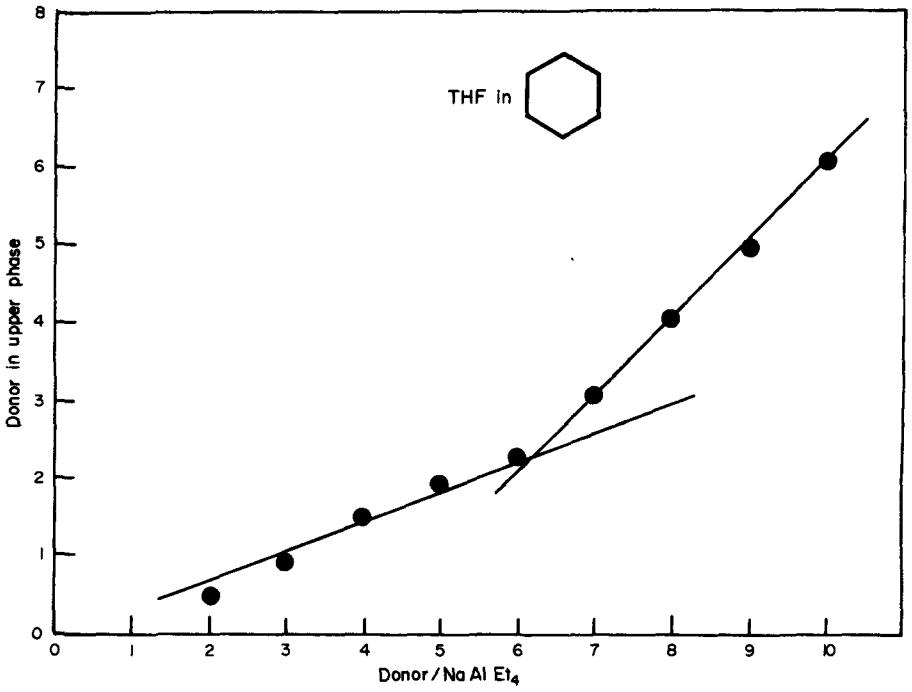

Fig. 1. Relative concentration of THF in the upper phase of the THF–$NaAlEt_4$–cyclohexane system as a function of the THF:Na^+ ratio.

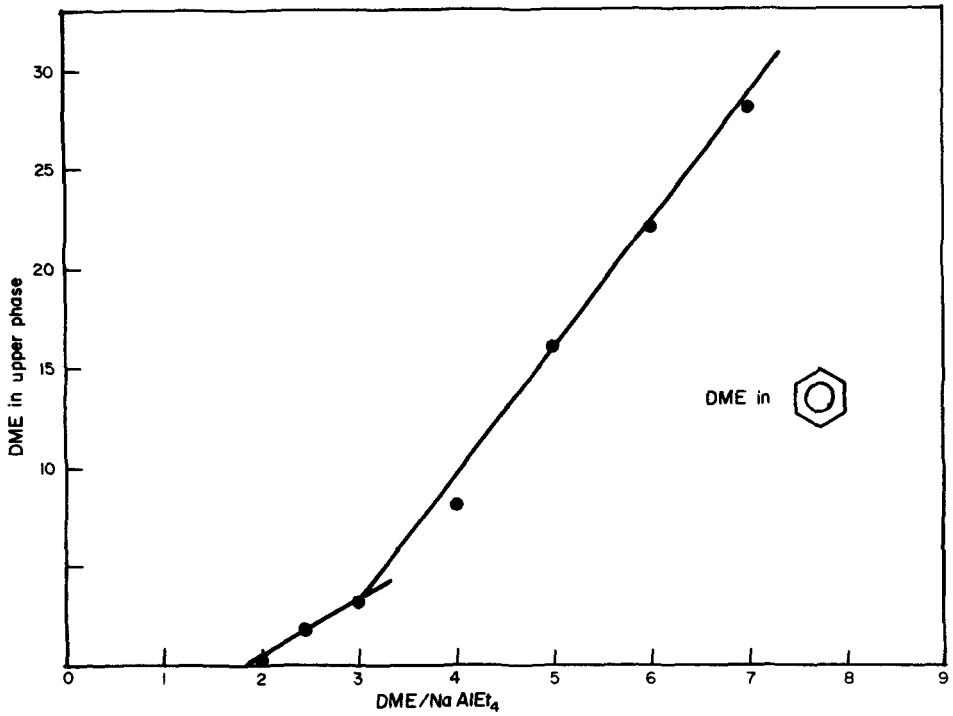

Fig. 2. Relative concentration of DME in the upper phase of the DME–$NaAlEt_4$–benzene system as a function of the DME:Na^+ ratio.

insolubility are all observed under particular conditions of solvent, donor, and D:Na^+ ratio. These results can be altered by using different salts. For instance, sodium tetra-*n*-butylaluminate ($NaAlBu_4$) forms two phases with DMSO in cyclohexane at D:Na^+ ratios where the $NaAlEt_4$ solvates are insoluble.

In Fig. 1, a typical plot is shown. Here the concentration of THF in the upper phase of the system $NaAlE_4$–cyclohexane–THF is observed to increase slightly with an increase in the ratio of THF:Na^+ until a ratio of 6:1 is reached, at which point a rapid concentration increase is noted. In Fig. 2, an analogous plot using dimethoxyethane (DME) as the donor in the system NaAlEt–benzene–DME can be seen. Here the break occurs at a ratio of 3:1, again supporting a value of six for the solvation number. Additional studies give the same results with dimethylsulfoxide (DMSO) and pyridine (py).

It is not unreasonable to expect both four and six as well as other less common values for the solvation number of the Na^+ ion depending on the donicity and geometry of the donor and, perhaps, the concentration[21]. However, of particular concern is the results obtained with THF as the donor. There is no reason to reject the solvation number of four obtained by both IR and ^1H NMR shifts, yet a value of six is clearly shown in this study. Most reasonably the discrepancies can be attributed to either (a) different sensitivieies of the various methods, or (b) the measurement of different quantities by the different methods. But regardless of the reasons, this calls into question the accepted methods for solvation number determination and, based on the observations reported here, it seems appropriate that the techniques which have generally been accepted as valid should be reevaluated.

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acetylacetone formed after CO abstraction from ketone.

All the chemicals used were either AR or CP grade. Literature methods have been used to prepare benzoylacetylacetone[13] and $Ru(PPh_3)_3Cl_3$ (ref. 14)

Preparation of $[RuCO(PPh_3)(CH_3COCH_2COCH_3)Cl_2$ — Mixed solution of $Ru(PPh_3)_3Cl_3$ (50 mg) in benzene (30 ml) and benzoylacetylacetone (50 mg) in ethanol (50 ml) was refluxed until the colour of the solution became green (6-8 hr) It was then evaporated to near dryness and the residue treated with ether whereby a green compound was obtained. It was twice recrystallized from ethanol and washed with ether. The complex, satisfactorily analysed for $[Ru(CH_3COCHCOCH_3)PPh_3COCl_2]$

The magnetic moment and the IR spectra (ν_{max} in cm^{-1}) of the ligand and the complex were recorded by the methods described earlier[15].

The IR spectrum of the complex shows all the characteristic bands of triphenylphosphine (3065, 1505, 1450, 1310, 1190, 1155, 1097, 1040, 1015, 750, 695, 530) Besides these, bands are also present at 1980, 1590, 1545 and 1395 The presence of a new band at 1980 is very interesting. It can be due to either ν(CO), ν(Ru-H) or ν(N ≡ N). The analysis shows that there is no nitrogen present in the complex and therefore nitrogen complex of ruthenium is ruled out. The presence of Ru-H bond is also highly improbable because its presence in the complex will raise the oxidation state of ruthenium to + 4 which may not be possible under the experimental conditions (Triphenylphosphine may act as reducing agent rather than oxidizing agent) Therefore we assign the band at 1980 to ν(CO). Since the positions of some of the bands in the complex match very well with those of the coordinated acetylacetone[16], it is assumed that it is the diketone, formed as a result of the decomposition of triketone, rather than triketone itself which is acting as a complexing ligand This is further supported by the microanalytical data of the complex Therefore bands at 1590, 1545 and 1395 are assigned to the presence of coordinated acetylacetonate The positions of the bands due to ν(C = O) of acetylacetonate undergo a bathochromic shift and appear at 1550-1600, indicating a strong interaction between the metal ion and ν(C = O) group of the acetylacetonate.

The analytical data suggest that the complex has one molecule each of triphenylphosphine, acetylacetonate ion, and carbonyl and two ions of chloride. Therefore the formula of the compound should be $RUCH_3COCHCOCH_3)(PPh_3)(CO)Cl_2$. Further ruthenium is present in the complex in + 3 oxidation state is indicated by the magnetic moment which corresponds to one unpaired electron.

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Studies on the Complexes of Some Heterocyclic Bases with Noble Metals

Vijay Kumar†, M. M. Haq‡ & Naseer Ahmad*

Department of Chemistry, Aligarh Muslim University Aligarh 202001

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Complexes of the chlorides of Ru(III), Rh(III), Pd(II), Pt(IV) and Au(III) with heterocyclic bases, *o*-toluidine, *o*-dianisidine and 2,2′-biquinoline have been synthesized. The metal : ligand ratio is found to be 1 : 2 in the cases of Ru(III), Rh(III), Pd(II) and Au(III) complexes with *o*-toluidine and *o*-dianisidine. Platinum forms 1 : 1 complexes with the two ligands. 2,2′-Biquinoline forms 1 : 1 complexes with all the metal ions. The IR and magnetic susceptibility data have been used to characterize the compounds.

A SURVEY of chemical literature showed that very little is known about complexes of Ru(III), Rh(III), Pd(II), Pt(IV) and Au(III) with the bases, *o*-toluidine, *o*-dianisidine and 2,2′-biquinoline We are reporting the preparation and characterization of these complexes.

o-Toluidine, *o*-dianisidine and 2,2′-biquinoline were E. Merck reagents. Chlorides of Ru(III), Rh(III), Pd(II), Pt(IV) (aq. HCl solution) and Au(III) (JMUK) were used to prepare the complexes

The ethanolic solutions of the metal salts and the ligands were mixed in the molar ratio of 1 2 with a slight excess of the ligand and the mixture was warmed on a water-bath for a few min The precipitate was cooled, centrifuged, washed with a little ether and then with large amounts of ethanol several times. The product, thus obtained was dried *in vacuo* at room temperature The

†Present address Chemistry Department, S V College, Aligarh 202001.

‡Present address Chemistry Department, Jamia Milia Islamia, New Delhi.

complexes were analysed for carbon, hydrogen and nitrogen by the usual methods Chloride was es i-mated as silver chloride

The analytical data (Table 1) of the complexes indicate that Ru(III), Rh(III), Pd(II) and Au(III) form 1:2 complexes with *o*-toluidine a id *o*-dianisi-dine Pt(IV) forms 1·1 complexes with all the ligands while 2,2′-biquinoline forms 1:1 complexes with all the metal ions Most of the complexes de-compose around 200°.

The molar conductance values of $10^{-3}M$ solutions of complexes in dimethyl sulphoxide show that the complexes of *o*-toluidine and *o* dianisidine w th Ru(III), Rh(III) and Au(III) and the 2,2′-biquinoline complex with Ru(III) are 1.1 electrolytes This indicates that one chloride is present outside the coordination sphere Since the molar conductance values for the Pd(II) and Pt(IV) complexes with *o*-toluidine and dianisidine and of Rh(III), Pd(II), Pt(IV) and Au(III) complexes with 2,2′-biquinoline are in the range 3·0-5·40 ohm^{-1} cm^2 mole^{-1}, these complexes are non-electrolytes

The magnetic moments of the Ru(III) complexes (Gouy method) of *o*-toluidine, *o* dianisidine and 2,2′-biquinoline show them to be paramagnetic with values of 1·92, 1·73 and 1·92 B.M, respectively whereas the rest of the complexes are dia-magnetic *o*-Toluidine and *o*-dianisidine have structures similar to benzidine and are expect-ed to act as bidentate ligands forming octa-hedral complexes with Ru(III) $[Ru(Bzd)_2Cl_2]Cl$, where benzidine acts as a bidentate ligand, is hexacoordinate and has a magnetic moment of 1 95 B M Ru(III) in dichlorobiquinolineruthenium (III) chloride is four-coordinate with a magnetic moment of 1·92 B M which shows it to be in a low spin state, an unknown phenomenon among tetrahedral complexes, since Δt is of lower magnitude than the energy for pairing of electrons It may, therefore, be supposed to be square planar

The Rh(III) complexes of *o* toluidine a id *o* di anisidine are low-spin octahedral complexes Octa-hedral complexes of Rh(III) have been observed[2] to be diamagnetic The rhodium(III) biquinoline complex, where biquinoline acts as a bidentate ligand and the three chlorides are inside the coordination sphere, is pentacoordinate and is an interesting example of coordination number five The Pd(II) and Pt(IV) complexes of *o* toluidine and *o*-dianisidine are hexacoordinate and diamagnetic as has been reported[2] in several other complexes of these metal ions The Au(III) complexes of *o*-toluidine and *o*-dianisidine contain six coordinate Au(III) which is a d^8 system This ion can be diamagnetic if the octahedron is a distorted one The biquinoline complexes of Pd(II), Pt(IV) and Au(III) are also expected to be diamagnetic[2] The Au(III)-biquinoline complex has been reported as pentacoordinate earlier[3]

The ligands, *o* toluidine, *o* dianisidine and 2 2′ bi-quinoline, are non-functional and have two similar coordination sites The IR spectra may decide

TABLE 1 — ANALYTICAL AND OTHER CHARACTERIZATION DATA OF COMPLEXES

Compound	Colour	Found (Calc), %				Λ$_M$ (ohm^{-1} m^2 mole^{-1})
		C	H	N	Cl	
RuL_2Cl_2 Cl	Bluish-b'ack	53 25 (53 21)	5 10 (5 10)	8 88 (8 88)	16 88 (16 82)	42 62
RhL_2Cl_2 Cl	Dirty yellow	52 96 (53 07)	5 02 (5 09)	8 85 (8 84)	16 82 (16 77)	40 28
PdL_2Cl	Yellow	55 91 (55 88)	5 34 (5 36)	9 32 (9 31)	11 80 (11 78)	4 ⁄4
$PtL\ Cl_4$	Greyish-green	30 62 (30 61)	2 91 (2 93)	5 09 (5 10)	25 82 (25 81)	3 08
AuL_2Cl_2 Cl	Dirty green	46 19 (46 20)	4 42 (4 43)	7 70 (7 70)	14 67 (14 61)	39 99
RuL'_2Cl_2 Cl	Blue	48 34 (48 32)	4 60 (4 63)	8 02 (8 05)	15 21 (15 27)	41 98
RhL'_2Cl_2 Cl	Dirty green	48 16 (48 19)	4 60 (4 62)	8 00 (8 03)	15 19 (15 24)	43 01
PdL'_2Cl_2	Dirty yellow	50 48 (50 52)	4 89 (4 84)	8 41 (8 42)	10 66 (10 65)	5 09
$PtL'Cl_4$	Dark violet	28 88 (28 89)	2 75 (2 77)	4 79 (4 82)	24 44 (24 39)	5 00
AuL'_2Cl_2 Cl	Blue	42 50 (42 46)	4 05 (4 07)	7 07 (7 07)	13 46 (13 43)	40 22
$RuL'Cl_2$ Cl	Green	46 60 (46 62)	2 59 (2 60)	6 05 (6 07)	22 90 (22 92)	38 90
$RhL''Cl_3$	Dirty yellow	46 39 (46 41)	2 57 (2 59)	6 00 (6 02)	22 82 (22 83)	4 00
$PdL''Cl_2$	Greenish yellow	49 82 (49 85)	2 75 (2 78)	6 45 (6 46)	16 36 (16 35)	3 25
$PtL''Cl_4$	Yellow	36 47 (36 43)	2 00 (2 03)	4 70 (4 72)	23 94 (23 90)	5 40
$AuL''Cl_3$	Dark orange	38 60 (38 63)	2 13 (2 16)	5 01 (5 00)	19 00 (19 00)	5 22

L = *o*-toluidine, L′ = *o*-dianisidine, L″ = 2 2′-biquinoline

whether the coordination occurs through both the sites or just one The coordination at only one position will perturb the vibrations of one end leaving those of the other end unaffected and consequently raising the number of bands in the IR spectra of the complexes as compared to those of the free ligands

The assignment of IR bands in the present study is based on those given by Rahman *et al* [4,5] for the present ligands

The νNH bands which occur at 3448 (m), 3322 (w), 3045 (w), and 2985 (w) cm $^{-1}$ in *o* toluidine go down in intensity and frequency on complexation Similarly the NH_2 bending vibrations [1625 (vs), 1575 (s) cm $^{-1}$] and νC—N vibrations [1333 (w), 1316 (s), 1289 (s), 1258 (s) cm $^{-1}$] of the ligand go down in intensity and frequency in the complexes The ring vibrations [1490 (vs), 1447 (m), 1370 (s) cm $^{-1}$] and NH_2 rocking [823 (s) cm^{-1}] in the ligand are also lowered in frequency The number of bands is reduced in a few cases but remains the same in most cases on chelation Hence it is concluded that coordination occurs at both the donor sites The same conclusion is drawn about the complexes of *o*-dianisidine

The bands at 840 (s), 837 (s), 787 (s), 763 (s) and 735 (s) cm^{-1} in 2,2′ biquinoline may be assigned to CH out of plane deformations These are reduced in number and intensity and are lowered in frequency on complexation The bands at 1592 (s), 1550 (m) and 1493 (s) cm $^{-1}$ in 2 2′-biquinoline may be assigned to C=C and C=N vibrations These bands also show a downward trend in frequency on complexation These shifts in frequency show that chelation occurs between Ru(III), Rh(III), Pd(II), Pt(IV) and Au(III) and 2,2′-biquinoline

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Some Reactions of Hexaaryldilead with Organoantimony(V) Compounds

S N Bhattacharya & A K Saxena*

Department of Chemistry University of Lucknow Lucknow 226007

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Interactions of hexaaryldilead, Ar_6Pb_2 (Ar = phenyl and *p*-tolyl) with triarylantimony -sulphides, -oxides, -dihalides and -dipseudohalide have been studied. The organoantimony(V) compounds are converted to triorganoantimony while the Pb-Pb bond of hexaaryldilead is cleaved to yield products like Ar_4Pb, Ar_2PbX_2 (X = Cl, Br or NCS).

THE relative reactivity of M M and M C bond of Gr IVB elements towards electrophilic reagents decreases in the order Si<Ge<Sn<Pb and has been successfully employed in the synthesis of many of their compounds[1] Hexaorganodilead compounds exhibit a higher order of chemical reactivity and thermal instability than the corresponding tetraorganolead compounds because of the presence of Pb-Pb bond[2].

Okawara and coworkers[3] have studied the reactions of some hexaorgano Gr(IV) M-M bond and reported that to a limited extent, sulphur insertion takes place in the Sn-Sn bond by triorganoantimony sulphides However, parallel reactions were not observed with Ge-Ge or Si-Si bonds Reaction of hexaphenyldilead with sulphur has been also reported to produce bis(triphenyllead)sulphide[4]

In the present communication we report some reactions of hexaaryldilead with triarylantimony sulphides, -oxides, -halides and -pseudohalides The comparative reactivity of $(SCN)_2$ and cynogen iodide to give pseudohalides have recently been reported from this laboratory[5,6]

Hexaaryldilead[7], hexaphenylditin[8], triarylantimony[9] and the corresponding triarylantimony sulphides[10], -oxides[11], -dihalides (Cl, Br)[12] and -dithiocyanate[13] were prepared by the reported methods Solvents were purified and dried before use Moisture was excluded wherever necessary

Some representative experiments are described below and further details are given in Table 1

(i) *Reaction of Ph_6Pb_2 with Ph_3SbS* — To a refluxing solution of Ph_6Pb_2 (0·876 g; 0 001 mol) in chloroform (50 ml) was added dropwise a chloroform solution of triphenylantimony sulfide (0 385 g, 0·001 mol) The reactants were refluxed for 4 hr and then filtered hot The filtrate was cooled after adding ethanol (1 ml) to crystallize out any unreacted hexaphenyldilead The filtrate was then evaporated and the residue extracted with hot pet ether The filtrate was concentrated to precipitate triphenylantimony (m p 48-49°) The residue after crystallization from CCl_4-pet. ether mixture yielded the bis(triphenyllead)sulphide, m p 138° (lit [6] m p 139°)

(ii) *Reactions of Ar_6Pb_2 (Ar = phenyl, p-tolyl) with Ar_3SbX_2 (Ar = Ph, p-tolyl, X_2 = Cl, Br, NCS)* — All the reactions were carried out in boiling $CHCl_3$ solution under identical conditions In a typical experiment, a solution of triphenylantimony dichloride was added dropwise to a solution of hexaphenyldilead in 1 1 molar ratio and the reaction mixture refluxed for 6-7 hr The solid thus separated was filtered off and identified as diphenyllead dichloride The filtrate was concentrated and the residue was fractionally crystallized giving tetraphenyllead and triphenylantimony

(iii) *Reaction of Ph_6Pb_2 with Ph_3SbO* — To a boiling solution of hexaphenyldilead (1·74 g, 0 002 mol) in chloroform was added a solution of Ph_3SbO (0·738 g, 0·002 mol) in chloroform during 30 min The reaction mixture was refluxed vigorously for 8 hr and filtered hot to separate diphenyllead oxide The solution was concentrated upto dryness and then extracted with benzene On cooling the solution tetraphenyllead (m p 226-27°) crystallized

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II. CHEMISTRY

Coordination Compoudns

STUDIES ON MIXED LIGAND COMPLEXES OF THALLIUM(I) HALIDES : INTERACTION OF THALLIUM(I) MONO- AND DIPHENYL THIOUREA HALIDES WITH 2, 2'-DIPYRIDYL AND 1, 10-PHENANTHROLINE

F. R. RAHMANI*, M. SAYEED, A. U. MALIK *and* N. AHMAD

Inorganic Research Laboratory, Chemistry Department, Aligarh Muslim University, Aligarh, U.P.

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Complexes of Thallium(I) halides with phenyl thiourea and diphenyl thiourea and their adducts with dipyridyl and o-phenanthroline have been synthesised and characterised with elemental analyses, m.p., molar conductance and infrared spectra. Thallium(I) forms mono or bicoordinate complexes (Pfeiffer & Werdelmann, 1950) with thioureas and still is capable of coordinating with strong coordinating agents to achieve higher coordination number.

Keywords : Thallium Halides; Complexation; Substituted Thioureas; Heterocyclic Amines.

INTRODUCTION

THE chemistry of Tl(I) has some resemblance with Ag(I) and Cu(I) as far as the behaviour of halides is concerned. Like Cu(I) and Ag(I), Tl(I) ion forms mono or bicoordinate complexes as reported by Pfeiffer and Werdelmann (1950) and Psheritsyn and Prokofena (1959) and still has ample room to accommodate some strong coordinating agent in order to achieve its coordination maximum.

EXPERIMENTAL

Reagents:

Monophenylthiourea (PTU), Diphenylthiourea (DPTU) and thallous chloride were all B. D. H. products. 1, 10-phenanthroline and 2, 2'-dipyridyl were Analar reagents.

Preparation of the Complexes:

To a 50 ml well stirred suspension of thallium(I) halide (2×10^{-1}M) in ethanol, 50 ml alcoholic solution of PTU/DPTU ($1\times10^{-1}M$) was added with constant shaking. The resulting mixture was warmed over a water bath for 5–10 minutes followed by intermittent stirring for about half an hour. The mixture was then centrifuged. The clear solution was separated for crystallization whereas the residue consisting mainly of Tl(I) halide was rejected. The solution was concentrated and left for crystallization. Crystals of the complex appeared after about 6 hours.

For the preparation of mixed ligand complexes, equimolar ethanolic solutions of Tl(I) halide-substituted thiourea complex and the heterocyclic amine were mixed

TABLE I

Chemical analyses and some characterizing data of thallium(I) complexes

	Compounds	Metal (%)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	M.Pt. °C	Λ M Ohm^{-1} cm^2 mole^{-1}
1.	Pentakis (PTU) Tl(I) chloride	20.45	41.06	3.96	13.98	152	32.5
	$C_{35}H_{40}ClN_{10}S_5Tl$	(20.11)	(41.34)	(3.93)	(13.78)		
2.	Chloropentakis (PTU) mono	18.44	46.28	4.12	13.84	124	12.8
	(dipy) thallium (I)	(17.43)	(46.07)	(4.09)	(13.33)		
	$C_{45}H_{45}ClN_{12}S_5Tl$						
3.	Chloropentakis (PTU) mono	17.14	46.64	4.24	14.48	132	8.4
	(o-phen) Thallium (I)	(17.08)	(46.15)	(4.01)	(14.04)		
	$C_{47}H_{45}ClN_{12}S_5Tl$						
4.	Pentakis (PTU) Tl(I) bromide	20.12	38.82	3.64	13.58	157	46.0
	$C_{35}H_{40}BrN_{10}S_5Tl$	(19.27)	(39.60)	(3.77)	(13.20)		
5.	Bromo Pentakis (PTU) mono-	16.25	43.76	3.88	13.84	102	18.5
	(dipy) Thallium (I)	(16.79)	(44.38)	(3.94)	(13.80)		
	$C_{45}H_{45}BrN_{12}S_5Tl$						
6.	Bromo Pentakis (PTU) mono-	16.84	44.94	3.72	13.56	138	7.6
	(o-phen) Thallium (I)	(16.47)	(45.46)	(3.84)	(13.54)		
	$C_{47}H_{45}BrN_{12}S_5Tl$						
7.	Mono (DPTU) Tl(I) chloride	43.84	32.64	2.28	5.96	155	22.7
	$C_{13}H_{12}ClN_2STl$	(43.65)	(33.32)	(2.56)	(5.98)		
8.	Chloro mono (DPTU) mono	31.25	44.52	3.18	8.98	135	3.4
	(dipy) Thallium (I)	(32.73)	(44.20)	(3.20)	(8.96)		
	$C_{23}H_{20}ClN_4STl$						
9.	Chloro mono (DPTU) mono	31.48	47.02	3.22	8.98	135	3.4
	(o-phen) Thallium (I)	(31.52)	(46.27)	(3.08)	(8.63)		
	$C_{25}H_2OClN_4STl$						
10.	Mono (DPTU) T(I) bromide	38.88	31.68	2.53	5.44	230	33.6
	$C_{13}H_{12}BrN_2STl$	(39.86)	(30.43)	(2.34)	(5.46)		
11.	Bromo mono (DPTU) mono	30.68	40.84	2.98	8.44	134	14.3
	(dipy) Thallium (I)	(30.55)	(41.26)	(2.99)	(8.37)		
	$C_{23}H_{20}BrN_4STl$						
12.	Bromo mono (DPTU) mono	24.52	42.82	2.84	8.12	180	6.7
	(o-phen) Thallium (I)	(24.49)	(43.30)	(2.88)	(8.08)		
	$C_{25}H_{20}BrN_4STl$						
13.	Bis (DPTU) Thallium (I) iodide	25.81	39.54	3.02	7.24	160	41.1
	$C_{26}H_{24}IN_4STl$	(25.93)	(39.59)	(3.04)	(7.10)		
14.	Iodo bis (DPTU) mono	21.24	45.26	3.44	8.82	142	8.4
	(dipy) Thallium (I)	(21.64)	(45.75)	(3.38)	(8.89)		
	$C_{36}H_{32}IN_6S_2Tl$						
15.	Iodo bis (DPTU) mono	20.94	47.44	3.46	8.62	175	5.9
	(o-phen) Thallium (I)	(21.10)	(47.09)	(3.30)	(8.67)		
	$C_{38}H_{32}IN_6S_2Tl$						

Calculated values are given in parenthesis.

PTU = phenyl thiourea, DPTU = Diphenyl thiourea, dipy = 2, 2′-dipyridyl o-phen = 1, 10-phenanthroline.

in equimolar proportion. The mixed ligand complex precipitated and settled down. The precipitate was separated and washed several times with alcohol and was finally dried in vacuo over CaO.

The C, H and N analyses were carried out by microanalytical laboratory of this department and Tl was estimated gravimetrically as given by Furman (1962).

The molar conductances of the complexes were measured in DMSO using a Philips Conductivity Bridge model PR 9500 with a dip type conductivity cell.

Infrared spectra were recorded with a Beckman IR-20 for the range 3–16 μ using KBr pellets and in the far infrared range (16–50 μ) using a Beckman IR 5A fitted with a CsBr prism and using nujol mulls.

Results and Discussion

1 : 5 and 1 : 1 complexes are formed by the interaction of Tl(I) halides and PTU and DPTU respectively with the exception of Tl(I) iodide which gives a 1 : 2 product with DPTU. The mixed ligand complexes are insoluble in water and common organic solvents.

All the Tl(I) halide-substituted thiourea complexes have molar conductances (1×10^{-3}M in DMSO) in the range of 22 to 46 ohm^{-1} cm^2 $mole^{-1}$ suggesting 1 : 1 electrolytic behaviour. Molar conductances of the mixed ligand complexes in DMSO (1×10^{-3}M) fall in the range of 3 to 18 ohm^{-1} cm^2 $mole^{-1}$ possibly indicating a non-electrolytic nature and therefore the formation of 8 and 4 coordinate complexes of the type Tl (o-phen or dipy) $(PTU)_5$ × and Tl (o-phen or dipy) (DPTU) X. .Geary (1971) has reported molar conductances for different electrolytes which have been used for comparison.

All the substituted thiourea complexes presumably show coordination through nitrogen which is inferred by the typical changes taking place in the regions of NH deformation and CN antisymmetric stretchings, C-S stretchings and the presence of a strong band at *Ca* 240 cm^{-1} assigned to Tl-N stretches. The i.r. spectra of the heterocyclic amines-substituted thiourea complexes show typical bands of coordinated amines as reported by Rahmani *et al.* (1976, 1977) earlier.

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Studies on Tetrakis(thiourea)nickel(II) Dichloride & Its Mixed Ligand Complexes

ABU SHAHMA, M. M. KHAN, N. AHMAD* & A. U. MALIK
Department of Chemistry, Aligarh Muslim University
Aligarh 202 001

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$[Ni(tu)_4]Cl_2$, $[Ni(tu)_2py_2]Cl_2$, $[Ni(tu)_2dipyCl]Cl$, $[Ni(tu)_2o$-phenCl]Cl and [Ni(tu)(PAA)(HPAA)Cl] (where tu = thiourea, py=pyridine, dipy=dipyridyl, *o*-phen=*o*-phenanthroline and HPAA=phenylarsonic acid) have been synthesised and characterised on the basis of their melting point, elemental analysis, colour, molar conductances, magnetic moment, infra red and electronic spectral and thermogravimetric data. $Ni(tu)_4Cl$ is a four-coordinated tetrahedral complex although it has been reported earlier as octahedral.

THE crystal and molecular structure of $Ni(tu)_4Cl_2$ has been studied at low temperature by Castro and Truter[1] who reported a distorted octahedral arrangement of four thioureas and two chlorides around Ni(II). Hare and Ballhausen[2] also studied this complex and found that the four sulphur atoms are present in a plane and the two chlorides occupy the two axial positions (*trans*). They also found an average magnetic moment of 3.04 B.M. However, on the basis of the studies described in the present paper, we propose that nickel is tetra-coordinated in this complex.

Thiourea(tu), 2,2'-dipyridyl (dipy), *o*-phenanthroline(*o*-phen), pyridine(py) and phenylarsonic acid (HPAA) used were AR grade chemicals. Thiourea was estimated potentiometrically using an $Ag\text{-}Ag_2S$ electrode as described earlier[3]. Amines were estimated *p*H-metrically using standard nitric acid as a titrant.

Preparation of nickel(II)-thiourea complex — To an ethanolic solutions of thiourea (1 g in 20 ml) was added an aqueous solution (0.5 g in 20 ml) of nickel (II) chloride (4 : 1 molar ratio with a slight excess of thiourea) containing a few drops of conc. HCl. The resulting solution was heated on a water-bath for 15 min and left to stand for 3-4 hr to get crystals of the complex. The crystals were washed with acetone and dried *in vacuo* over CaO.

Preparation of nickel(II)-thiourea mixed ligand complexes—To an aqueous solution of the nickel (II)-thiourea complex (1 g in 20 ml) was added pyridine (5 ml) and acetone (50 ml). The solution was filtered and the filtrate refluxed for 2 hr. The refluxed solution was allowed to stand and after three days, crystals of the complex appeared.

A similar procedure was adopted for the preparation of the substituted nickel thiourea complexes with 2,2'-dipyridyl and *o*-phenanthroline. In the case of phenylarsonic acid, a yellow product was obtained after heating the solution. It was separated by filtration, washed several times with ethanol, acetone and dried *in vacuo*.

The complexes are soluble in ethanol, dimethylformamide and nitromethane and sparingly soluble in acetone. The phenyl arsonic acid complex is insoluble in organic solvents but slightly soluble in water.

The thermograms of the complexes were taken between ambient and 500° temperatures at R. R. L Hyderabad. The magnetic susceptibility measurements were made with a Faraday balance at B. H. U., Varanasi and Evan's NMR method[4]. The λ_{max} values of the various complexes were determined by applying Vosburgh and Cooper's method[5].

The IR spectra of the complexes were recorded on a Perkin Elmer 237 spectrometer in the region 2.5 to 15μ using KBr discs. The far IR spectra (16 to 40 μ) were taken on a Perkin Elmer IR-10 spectrometer in nujol mull.

The elemental analyses of the complexes are shown in Table 1. Castro and Truter[1] assigned a distorted octahedral geometry to tetrakis(thiourea) nickel(II)

TABLE 1 — CHARACTERISATION DATA OF THE COMPLEXES

Complex	Found (Calc.),%					Colour	m.p (°C)	μ_{eff} (B.M.)
	C	H	N	Cl	Ni			
$[Ni(tu)_4]Cl_2$ $(C_4H_{16}Cl_2N_8NiS_4)$	10.9 (11.07)	3.7 (3.71)	25.9 (25.81)	16.4 (16.33)	13.4 (13.52)	Yellowish-green	225	*3.23
$[Ni(tu)_2Py_2]Cl_2$ $(C_{12}H_{18}Cl_2N_6NiS_2)$	30.9 (32.73)	3.8 (4.12)	19.2 (19.08)	16.1 (16.10)	13.3 (13.33)	Bluish-green	360	2.89
$[Ni(tu)_2dipyCl]Cl$ $(C_{12}H_{16}Cl_2N_6NiS_2)$	32.3 (32.90)	3.7 (3.68)	19.0 (19.11)	16.3 (13.19)	13.3 (13.40)	Pink	210	2.18
$[Ni(tu)_2$-o-phenCl]Cl $(C_{14}H_{16}Cl_2N_6NiS_2)$	35.8 (36.39)	3.7 (3.49)	17.0 (18.19)	15.4 (15.35)	12.6 (12.71)	Dark-pink	319	1.47
[Ni(tu)(PAA)(HPAA)Cl] $(C_{13}H_{17}As_2ClN_2NiO_6S)$	27.1 (27.28)	3.4 (2.99)	4.9 (4.84)	6.2 (6.18)	10.4 (10.24)	Yellowish-Green	—	3.86

dichloride and Hare and Ballhausen[2] found four sulphur atoms in a plane and the two chlorides occupying the apical positions, confirming the six coordination number of nickel in the complex. Contrary to this report, we find nickel to be tetracoordinated with the two chlorides outside the coordination sphere in solution. The molar conductances of the complex in $10^{-3}M$ dilution in dimethyl sulphoxide, dimethylformamide and methanol are 73.2, 86.0 and 161.5 ohm^{-1} cm^2 $mole^{-1}$ respectively, whereas the molar conductances of nickel dichloride in these solvents at the same dilution are 62.0, 86.0 and 152.0 ohm^{-1} cm^2 $mole^{-1}$ respectively. The values are quite comparable and lead to the conclusion that the two chlorides are outside the coordination sphere in solution. The molar conductances of the mixed ligand complexes with pyridine, dipyridyl and *o*-phenanthroline are 62.0, 36.0 and 24.7 in DMSO, 86.0, 67.4, and 73.2 in DMF, 209.0, 114.0 and 73.2 ohm^{-1} cm^2 $mole^{-1}$ in methanol respectively indicative of their 1 : 2, 1 . 1 and 1 : 1 electrolytic nature respectively. These compounds may be formulated as : $[Ni(tu)_2py_2]Cl_2$, $[Ni(tu)_2dipyCl]Cl$ and $[Ni(tu)_2o\text{-phen}Cl]Cl$.

$[Ni(tu)_4]Cl_2$ has a magnetic moment of 3.23 B.M. in solid state and a moment of 2.86 B.M. in solution. The magnetic moments of $[Ni(tu)_2py_2]Cl_2$, [Ni(tu) (PAA) (HPAA)Cl] are 2.89 and 3.86 B.M. respectively. These three complexes are thus tetrahedral. This geometry is preferred to square-planar due to the spin-pairing energy and the minimization of electrostatic repulsion energy. The ground state term in tetrahedral nickel(II) complexes, $^3T_1(F)$, is orbitally triply degenerate and therefore the magnetic moments of such complexes may contain some orbital contribution. When the symmetry is lowered, there is less orbital contribution[6,7]. The orbital contribution may raise μ_{eff} to 4.1 B.M., but effects of covalency and/or of distortion may bring down the values as seen in [Ni(tu) (PAA) (HPAA)Cl]. $[Ni(tu)_2dipy Cl]Cl$ and $[Ni(tu)_2o\text{-phen}Cl]$ Cl have magnetic moments of 2.18 and 1.47 B. M. respectively. Divalent nickel has been reported to form chelated tetrahedral complexes[8] and also mixtures of tetrahedral and square-planar complexes in the same crystal[9]. The various proportions of the diamagnetic planar and the paramagnetic tetrahedral species in the same crystal can lead to μ_{eff} values of 0 to 4.1 B.M. Thus, the nickel(II) complex with *m*-chloro-*p*-phenylazo salicyladehyde shows a magnetic moment of 1.96 B.M. which has been explained to be due to a mixture[10] of planar and octahedral species of the same composition. Magnetic moments of a number of other Ni(II) complexes have been similarly explained on the basis of occurrence of mixtures of different stereochemistries in the same complex[11-13].

The thermogram of $[Ni(tu)]_4Cl_2$ shows removal of one, two, three and four thiourea molecules at 210°, 260°, 360° and 476°C respectively (Table 2). At 580°C, finally, the formation of metallic nickel occurs. In $[Ni(tu)_2Py_2]Cl_2$, the two thiourea molecules are removed at 234° and then elimination of pyridine occurs. This is substantiated by the absence of νC—S in the IR spectrum of $[Ni(tu)_2py_2]Cl_2$ which was previously heated to 250°. In the [Ni(tu)(PAA)(HPAA)Cl]complex, the loss of the phenyl arsonic acid (HPAA) is complete at 265° but the elimination of the phenyl arsonic acid anion (PAA^-) starts at 480° which seems quite plausible because of the involvement of ionic bonding.

TABLE 2 — THERMOGRAVIMETRIC ANALYSES

Complex	Temp (°C)	Wt loss, % Obs (theor)	Possible elimination of
$[Ni(tu)_4]Cl_2$	210	17.5 (17.54)	1 tu
	260	35.0 (35.07)	2 tu
	360	51.0 (52.0)	3 tu
	476	70.0 (70.14)	4 tu
	580	84.0 (86.48)	If Ni is formed
$[Ni(tu)_2py_2]Cl_2$	234	36.5 (34.57)	2 tu
	290	57.0 (52.54)	1 py
	435	63.0 (70.51)	2 py
$[Ni(tu)_2dipyCl]Cl$	280	34.0 (34.75)	2 tu
	426	70.0 (70.41)	1 dipy
$[Ni(tu)_2$-*o*-phen$Cl]Cl$	320	32.5 (32.95)	2 tu
	370	57.5 (64.14)	1 *o* phen
[Ni(tu)(PAA)(HPAA)Cl]	265	36.5 (32.26)	1 HPAA
	360	50.0 (54.05)	1 tu
	480		loss of $(PAA)^-$ begins

The IR spectra of $[Ni(tu)_2py_2]Cl_2$, $[Ni(tu)_2dipyCl]Cl$ and $[Ni(tu)_2$-*o*-phen$Cl]Cl$ were studied in the range 1600-200 cm^{-1} in comparison to the IR spectrum of $[Ni(tu)_4]Cl_2$. No pronounced changes were seen in the case of $[Ni(tu)_2py_2]Cl_2$ but in the spectra of $[Ni(tu)_2dipyCl]$ Cl and $[Ni(tu)_2$-*o*-phen$Cl]Cl$, bands typical of coordinated dipy and *o*-phen occur and shifting of frequencies due to coordinated thiourea is less pronounced in comparison to that in the case of $[Ni(tu_4)]Cl_2$ complex. The latter shows appreciable shifting in the region of NH_2 bending, NCN stretching and NH_2 rocking modes. These observations indicate that there is stronger bonding through the heterocyclic nitrogen in comparison to sulphur. This is also corroborated by the pattern of decomposition seen in thermograms where tu is eliminated earlier than py, dipy or *o*-phen. The strong bands observed at 280, 275, 265 and 270 cm^{-1} in the complexes, $[Ni(tu)_4]^{2+}$, $[Ni(tu)_2Py_2]^{2+}$ $[Ni(tu)_2dipyCl]^+$ and $[Ni(tu)_2$-*o*-phen$Cl]^+$ respectively are assigned to νM—S mode[14].

The electronic spectra of $[Ni(tu)_4]^{2+}$, $[Ni(tu)_2py_2]^{2+}$, $[Ni(tu)_2dipyCl]^+$ and $[Ni(tu)_2$-*o*-phen$Cl]^+$ show bands at 14705, 19305, 19230 and 19230 cm^{-1} respectively which are due to *d-d* transitions, with ε values of 11, 5, 3 and 8 respectively. The distinction between the square-planar and tetrahedral species is blurred in the solution state because of equilibrium between

the two species in the case of the latter three complexes. The bands at 25000, 25640, 28140 and 28570 cm^{-1} in these complexes respectively are assigned to charge transfer arising from M- L transition whereas the bands at still higher energies viz., 38480 in $[Ni(tu)_2py_2]^{2+}$, 32250, 37730 and 40000 in $[Ni(tu)_2dipyCl]^+$ and 37040, 42560 in $[Ni(tu)_2$-*o*-phenCl$]^+$ are L→M charge-transfer bands. The λ_{max} values for $[Ni(tu)_4Cl_2]$, $[Ni(tu)_2py_2]Cl_2$, $[Ni(tu)_2dipyCl]Cl$ and $[Ni(tu)_2$-*o*-phenCl$]Cl$ are 25000, 38460, 32250, 37040 cm^{-1} with $\epsilon = 24$, 8.4×10^3, 40×10^4 and 7.0×10^4 respectively. The $10D_q$ values for these complexes (in the same order) are 17505, 22107, 22170 and 22107 cm^{-1}.

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Inorganic Chemistry

KINETICS OF THE SUBSTITUTION REACTIONS OF SQUARE PLANAR COMPLEX, $Pd(THIOUREA)_4Cl_2$ WITH HETEROCYCLIC AMINES

A. U. MALIK, N. AHMAD, ABU SHAHMA *and* M. M. KHAN

Department of Chemistry, Aligarh Muslim University, Aligarh 202 001, India

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The kinetic studies on the substitution reactions of square planar metal complexes have been an area of extensive research for the last two decades. The main bulk of the recent work has been limited to Ni(II) group metals, namely Ni, Pd and Pt by Basolo *et al.* (1960, 1961), Malik (1972), Bekker and Robb (1975), and Coe and Rispoli (1976). Interesting correlations have been put forward between reactivities of the replaceable ligands and the rate of reactions. The mechanism of the substitution reactions has been explained on the basis of a two term rate law. The mechanism of the substitution reactions involving amino acids in the square planar complex, $[Pd(tu)_4]Cl_2$ (tu = Thiourea) has been reported by Farooq and Malik (1972).

The work described in this communication deals with the kinetic studies on the interaction of heterocyclic amines with tetrakis thiourea palladium(II) chloride using spectrophotometric and potentiometric methods of analysis.

Keywords: Palladium (II); Thiourea; Amines; Kinetics of Substitutions of Thiourea by Amines.

EXPERIMENTAL

Reagents

Palladium chloride (Johnson Matthey product) was used for the preparation of the thiourea complex. Thiourea (tu), o-phenanthroline (o-phen) and 2,2′ dipyridyl (dipy) were analytical grade products. 2-,3- and 4-picolines, 2,4- and 2,6-lutidines were reagent grade chemicals and were further purified by distillation. The aqueous solutions of the amines were standardized by *p*H metric titrations against standard nitric acid using calomel and glass electrodes.

The preparation of tetrakis thiourea palladium(II) chloride has been described previously.

The spectrophotometric and potentiometric measurements were carried out using Bausch and Lomb Spectronic '20' colorimeter and '*Kaycee*' potentiometer respectively.

In all the experiments, a constant ionic strength of 0.1M was maintained using KCl solution. The *p*H of the reactant mixture was kept at 6.5–7.0 using sodium acetate-acetic acid buffers.

KINETIC MEASUREMENTS

(*i*) *Spectrophotometric Methods*

The λ max. of the complex, $[Pd(tu)_4]Cl_2$ was observed at 360 mμ. For the systems $[Pd(tu)_4]Cl_2 + L$ (where L is a heterocyclic amine), the selection of the

wave length was made at 600 mμ. All spectrophotometric measurements were made in a manner similar to that described previously for $[Pd(tu)_4]Cl_2$-amino acid systems by Farooq and Malik (1972). The plot of

$$\log [(OD)_\infty - (OD)_0]/[(OD)_\infty - (OD)_t] \text{ vs.}$$

time t, gives a straight line (Fig. 1). For 2,4- and 2,6-lutidines, it was found that precipitates formed almost immediately after achieving maximum absorbance. The k_{obs} values are summarised in Table I and II.

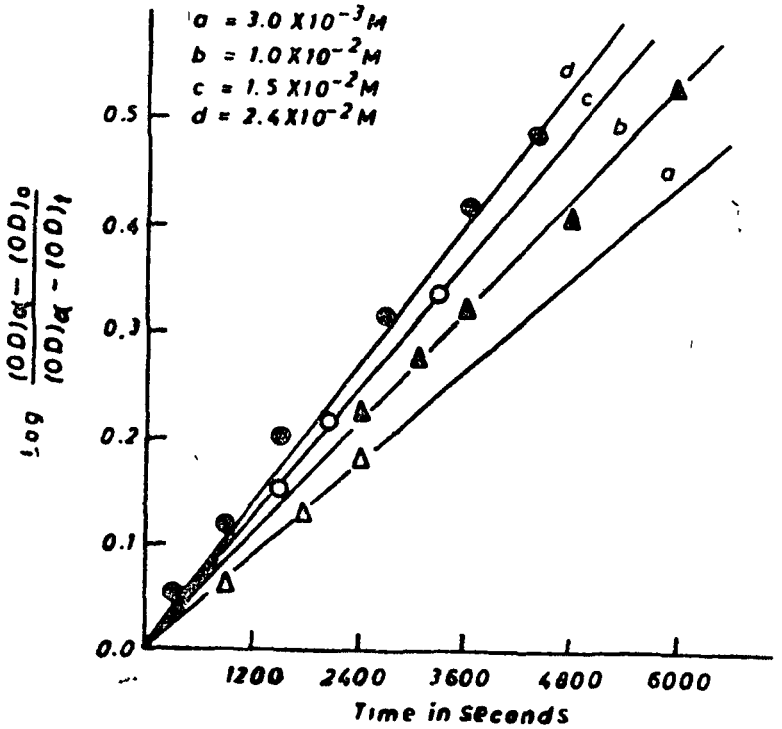


FIG. 1. Concn. of Pd $(tu)_4Cl_2$ = 1.0×10^{-3} M.

TABLE I

Values of K_{obs} at various pyridine concentrations (in presence of 0.1M KCl)

Temperature °C	Concn. of the complex $[Pd(tu)_4]Cl_2$ in M	Concn. of py in M	$k_{obs} \times 10^{-5}$ s^{-1}
20	1×10^{-3}	1.0×10^{-2}	3.6
,,	,,	1.6×10^{-2}	4.1
,,	,,	2.1×10^{-2}	4.8
25	,,	3.0×10^{-3}	3.2
,,	,,	1.0×10^{-2}	3.9
,,	,,	1.5×10^{-2}	4.3
,,	,,	2.4×10^{-2}	5.1

TABLE II

Values of k_{obs} for picolines and lutidines (in presence of 0.1M KCl)

Temperature °C	Concn. of the complex $[Pd(tu)_4]Cl_2$ in M	Concn of Amine in M	$k_{obs} \times 10^{-5}$ s^{-1}
25	1.0×10^{-3}	1.0×10^{-2} (2-picoline)	6.2
"	"	1.0×10^{-2} (3-picoline)	1.4
"	"	1.0×10^{-2} (4-picoline)	1.7
"	"	1.0×10^{-2} (2,4-lutidine)	3.4
"	"	1.0×10^{-2} (2,6-lutidine)	4.0

(*ii*) *Potentiometric Method*

The kinetics of the substitution reactions involving tetrakis thiourea palladium(II) chloride and heterocyclic amines were also studied potentiometrically. The theoretical aspects and experimental verifications of this method have been discussed while reporting the kinetics of the interaction of heterocyclic amines with tris thiourea copper(I) iodide (Malik & Khan, 1971). In brief, the potentiometric method is based upon the fact that there could exist a linear relationship between the concentration of thiourea and e.m.f. using Ag-Ag_2S as an indicator electrode in the *p*H range of 5–8. Taking advantage of this characteristic of Ag-Ag_2S electrode reported by Malik and Khan (1971), the first order rate reaction was determined by plotting $\log \frac{E_t}{E_\infty - E_t}$ *vs.* t, where E_∞ and E_t are the e.m.f. values at equilibrium and at time t respectively (Malik & Khan, 1973). The method was applied to the systems $[Pd(tu)_4]Cl_2$ + Py, $[Pd(tu)_4]Cl_2$ + picoline, $[Pd(tu)_4]Cl_2$ + dipy. and $[Pd(tu)_4]Cl_2$ + o-phen.

The plots of $\log \frac{E_t}{E_\infty - E_t}$ *vs.* t were found to be linear (Fig. 2), the k_{obs} values which are summarized in Tables I and II were obtained by multiplying 2.3 times the slope of the linear plots

$$k_{obs} = \frac{2.3}{t} \log \frac{E_t}{E_\infty - E_t}$$

RESULTS AND DISCUSSION

The kinetics of the substitution reactions of tetrakis (thiourea) palladium(II) chloride with pyridine, picoline, o-phenanthroline and dipyridyl were studied by spectrophotometric and potentiometric methods.

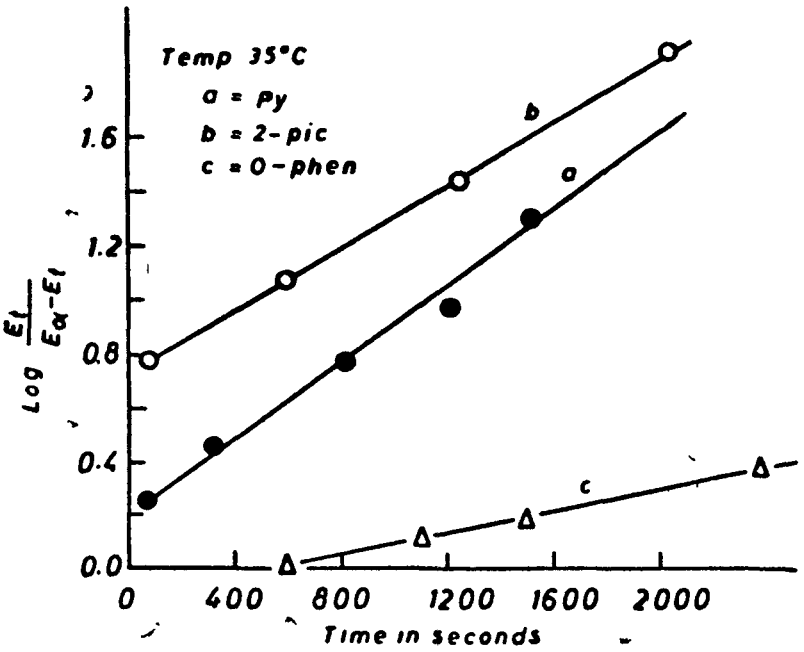


FIG. 2. Concentration of amine = 2.5×10^{-3} M.

The results of kinetic studies can be described by the equation (Basolo *et al.*, 1961; and Malik & Khan, 1971)

$$k_{obs} = k_1 + k_2 [Y] \qquad ...(1)$$

Equation (1) is equivalent to general rate law equation for ligand substitution in square planar metal complexes

$$\text{Rate} = k_1 + k_2 [Y] [\text{Complex}]$$

where k_1 and k_2 are first and second order constants respectively and Y is the entering group.

The equation (1) is valid for the present reaction study e.g., reaction of $[Pd(tu)_4]Cl_2$ with pyridine and related compounds. The reaction involves the displacement of one or more thiourea molecules in the complex, $[Pd(tu)_4]Cl_2$ by heterocyclic amine molecule. The values of k_{obs} are given in Tables I and II for pyridine, 2-, 3- and 4-picolines and lutidines. The values of k_{obs} *vs.* Y plotted for heterocyclic amines at 35 °C are given in Fig. 3. The plots are straight lines with slopes equal to k_2 and intercept equal to k_1.

The two term rate law applicable in this case requires a two step mechanism which has been proposed for ligand substitution in square planar complexes by Basolo and Pearson (1968).

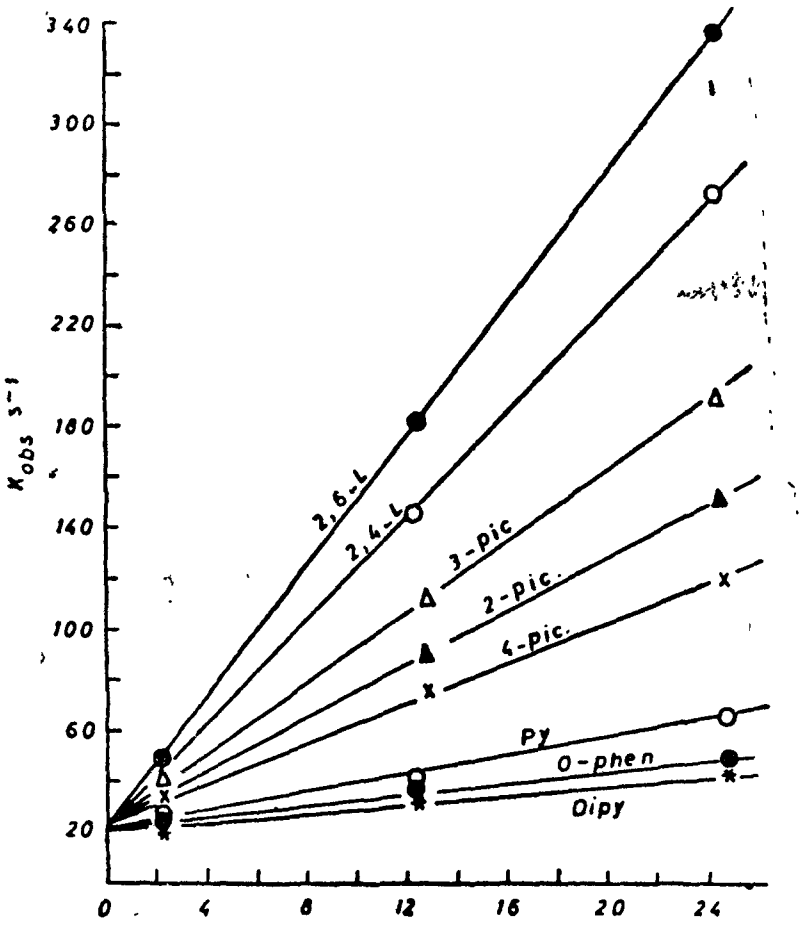
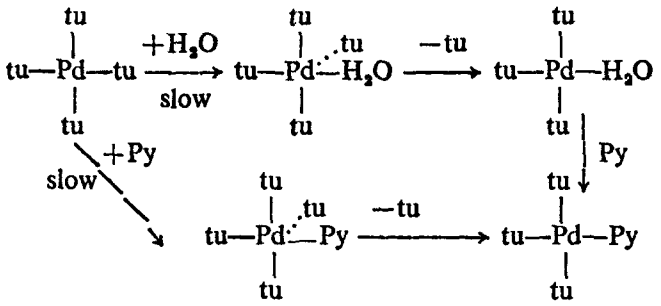


FIG. 3. Concentration of amine 1×10^{-3} M.



The rate constant k_1 is reponsible for slow displacement of thiourea by water which is then readily replaced by pyridine where k_2 is simply a direct bimolecular SN_2 reaction between the incoming ligand pyridine and the complex, $[Pd(tu)_4]Cl_2$. The effectiveness of pyridine as an incoming ligand is explained on the basis of

TABLE III

Comparison of rate of reactions of $Pd(tu)_4Cl_2$ *with various heterocyclic amines in aqueous solution at* 25 *and* 35 °C (*in presence of* 0.1*M KCl*)

Temperature °C	Concn. of the complex $[Pd(tu)_4]Cl_2$ in M	Concn. of Amine in M	$k_{obs} \times 10^{-5}\ s^{-1}$
25	1.0×10^{-3}	1.0×10^{-2} (py)	4.2
,,	,,	1.0×10^{-2} (2-pic)	6.4
,,	,,	1.0×10^{-2} (3-pic)	1.3
,,	,,	1.0×10^{-2} (4-pic)	1.5
,,	,,	1.0×10^{-2} (2,4-lutidine)	3.2
,,	,,	1.0×10^{-2} (2,6-lutidine)	4.2
35	5×10^{-4}	2.5×10^{-2} (py)	28.0
,,	,,	1.25×10^{-2} (py)	39.0
,,	,,	2.5×10^{-2} (py)	67.0
,,	,,	2.5×10^{-2} (2-pic)	40.6
,,	,,	1.25×10^{-2} (2-pic)	88.0
,,	,,	2.5×10^{-2} (2-pic)	151.0
,,	,,	2.5×10^{-2} (3-pic)	43.0
,,	,,	1.25×10^{-2} (3-pic)	113.0
,,	,,	2.5×10^{-2} (3-pic)	190.0
,,	,,	2.5×10^{-2} (4-pic)	34.0
,,	,,	1.25×10^{-2} (4-pic)	71.2

(*Continued*)

TABLE III (*contd.*)

Temperature °C	Concn. of the complex $[Pd(tu)_4]Cl_2$ in M	Concn. of Amine in M	$k_{obs} \times 10^{-5}\ s^{-1}$
"	"	2.5×10^{-2} (4-pic)	19.0
"	"	2.5×10^{-2} (2,4-*L*)	43.0
"	"	1.25×10^{-2} (2,4-*L*)	146.0
"	"	2.5×10^{-2} (2,4-*L*)	268.0
"	"	2.5×10^{-2} (2,6-*L*)	50.0
"	"	1.25×10^{-2} (2,6-*L*)	181.0
"	"	2.5×10^{-2} (2,6-*L*)	340.0
"	"	2.5×10^{-2} (dipy)	21.7
"	"	1.25×10^{-2} (dipy)	33.2
"	"	2.50×10^{-2} (dipy)	41.80
"	"	2.5×10^{-2} (o-phen.)	22.70
"	"	1.25×10^{-2} (o-phen.)	37.20
"	"	2.50×10^{-2} (o-phen.)	43.5

$d_\pi - p_\pi$ bond formation with the metal and thus stabilising the transition state by the formation of π-bond using 4*d* electrons of Pd(II).

A comparison of the k_{obs} values for the system : $[Pd(tu)_4]Cl_2$ + Amine (*vide* Tables I, II and III) evaluated from spectrophotometric as well as potentiometric methods reveals the following order for the various heterocyclic amines :

2-pic > 2,6L > py > 2,4L > 4-pic > 3-pic.
(spectrophotometric)

2,6L > 2,4L ~ 3-pic > 2-pic > 4-pic > py > o-phen > dipy.
(potentiometric)

It is not possible to correlate the k_{obs} values with those of the pK's of the substituent ligands, which follow the following order (Klinsberg, 1961)

$$\text{o-phen} \geqslant \text{2,4L} > \text{2,6L} > \text{4-pic} > \text{2-pic} > \text{3-pic} > \text{py}.$$

However, it must be emphasised that basicity would be of little importance in such reactions and polarizability plays a determined role in the activity of nucleophile (Belluco *et al.*, 1965). On the basis of present studies, it is also not possible to make a quantitative correlation between k_{obs} values and nucleophilic reactivities, however, in alkyl pyridines under study, the nucleophiles are reported to be almost of the same order.

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Selective Spectrophotometric Determination of Uranium(VI) Using Salicylaldimine Antipyrine

S A Nabi*, A R Siddiqi, M Athar, and N Ahmad

Dept of Chemistry, Aligarh Muslim University, Aligarh 202001, India

Selektive spektralphotometrische Bestimmung von Uran(VI) mit Hilfe von Salicylaldimin-antipyrin

Key words: Best von Uran(VI), Spektralphotometrie, Salicylaldimin-antipyrin

Various methods studied for the determination of uranium(VI) have been found to suffer from serious interferences by accompanying ions We therefore developed a spectrophotometric μg method using salicylaldimine antipyrine as a reagent This method offers the advantage that uranium can conveniently be determined without prior separation from other elements The yellowish complex formed is stable for more than 2 h in the approximately neutral solution (pH 6–7) The maximum absorption is at 410 nm Beer's law is obeyed in the range of 5–33 μg/ml The molar composition of the complex has been found to be 1 1 The stability constant is $4\,751 \times 10^4$ The standard deviation was determined to be 1 407 and 1 293 for 95 μg and 190 μg of U, respectively The interfering effect of numerous ions was examined In case of 50 μg of U the following limits of tolerance were found 150 μg of Fe^{3+}, 200 μg of Cu^{2+}, Ni^{2+} Co^{2+}, Mn^{2+}, Cr^{3+}, molybdate, phosphate, sulphate, iodate tungstate, oxalate, tartrate, citrate, thiocyanate, bromate chlorate, 500 μg of Cd^{2+}, VO^{2+}, Y^{3+}, Al^{3+}, 1,000 μg of Zn^{2+}, La^{3+}, Ce^{3+}, Th^{4+}, Zr^{4+}, Pt^{4+}, Na^+, Ba^{2+}, Sr^{2+} Ca^{2+}, Mg^{2+}, Pb^{2+}, Ag^+, In^{3+}, Hg^{2+}, Bi^{3+}, Sn^{4+} K^+ Sb^{3+}, Fe^{2+}, 2,000 μg of chloride, bromide, iodide, acetate

Working Procedure Add 0 2 ml of the sample solution to 3 ml of the reagent (see below), shake well, make the volume up to 10 ml with ethanol and measure the absorbance at 410 nm against a reagent blank prepared under the same conditions – *Reagent* This is prepared by mixing 1 mole of salicylaldehyde with 1 mole of 4-amino-antipyrine dissolved in ethanol The mixture is refluxed for 4 h, allowed to cool, concentrated and kept for slow cooling The crystals obtained are recrystallized from ethanol Melting point of the product is 197–198°C A 0 001 M solution in ethanol is prepared

* To whom correspondence should be addressed

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Ion-Selective Electrode for $Co(en)_3^{3+}$ Ions

I P Saraswat, S K Srivastava*, and A K Sharma

Dept of Chemistry, Univ of Roorkee, Roorkee-247672, India

Ionenselektive Elektrode für $Co(en)_3^{3+}$-Ionen

Key words: Best von Kobalt, Elektroden, ionenselektive, Ethylendiaminkomplex

* Address for correspondence

Epoxy resin based membranes of chromium ferrocyanide gel saturated with $[Co(en)_3]^{3+}$ ions have been prepared and used as an ion-selective electrode for the measurement of the activity of $[Co(en)_3]^{3+}$ ions (en = ethylenediamine) The response time of the membranes is less than a minute and the potentials generated are reproducible and remain constant for more than 4 h The standard deviation is ±0 34 mV for the concentration range of 10^{-1} to 10^{-4} M at pH 3 5 to 6 5 The electrode can be used for two to three months and no drift in potentials or validity range is observed upto this time Selectivity coefficient values in presence of a number of foreign ions are listed in Table 1, which show that the membrane is selective to $[Co(en)_3]^{3+}$ ions and there is practically no interference of other cations [3]

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Studies on the Complexes of Platinum Group Metals with Nicotinamide and Brucine

ABU SHAHMA, NASEER AHMAD
and
ANEES UDDIN MALIK

Chemistry Department Aligarh Muslim University,
Aligarh 202 001

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THE present communication reports the complex formation of platinum group metals with nicotinamide and brucine which finds little mention in the existing chemical literature.

Experimental

Na_2PtCl_4, Na_2PdCl_4, Na_2OsCl_6, Na_2IrCl_6 and $RhCl_3.H_2O$ (Jonnson Matthey), nicotinamide (B.D.H) and brucine (Whiffen) were used in these experiments.

The metal-nicotinamide (or metal-brucine) complexes were prepared by mixing the ethanolic solutions of the metal salt and the ligand, with vigorous shaking when a precipitate was obtained. It was washed several times with ethanol and subsequently with hexane and then dried *in vacuo*. The complexes were found to be insoluble in common organic solvents making their crystallization impossible.

The complexes were microanalysed for carbon, hydrogen, nitrogen and chlorine. The hydrogen analyses are somewhat high because of the ready absorption of water by these complexes during the process of analysis. The molar conductance was measured on a Philips conductivity bridge model PR 9500 in dimethyl sulphoxide using $1 \times 10^{-3} M$ solutions Table 1.

The infra red spectra of the complexes were recorded on a 'Perkin-Elmer' model '621' ir machine in the frequency range of 4000-600 cm^{-1} in KBr pellets. The magnetic susceptibility was measured on a Faraday balance at B.H.U., Varanasi. The thermograms were run on a manual apparatus at G.N.D. University, Amritsar and the diffused transmittance spectra were taken in nujol mull on NIR-vis-DMR-21 apparatus at RSIC, Madras.

Results and Discussion

The elemental analysis of the complexes shows that Pd(II) and Pt(II) interact with nicotinamide to give complexes with the composition, $Pd(Nicotinamide)_2Cl_2$ and $Pt(Nicotinamide)_2Cl_2$. The molar conductance[1] shows that they are non-electrolytes.

Nicotinamide absorbs at 3360, 3160 (NH bands), 1670 (CO stretching), 1610 and 1595 (C=C and C=N stretchings), 1115 (νCN) and at 1020 and 696 cm^{-1} (pyridine ring vibrations). The CO frequency goes down by 10-15 cm^{-1} on complexation. The $\nu C=C$ and $\nu C=N$ go to 1600, 1586, 1585 and 1525 cm^{-1} in Pd and Pt complexes respectively. The pyridine ring vibrations occur at 1020 and 682, and at 1000 and 640 cm^{-1} in Pd and Pt complexes respectively and show a great decrease in intensity. The NH bands at 3360 and 3160 cm^{-1} show splitting into several peaks in the two complexes. These changes in the ir absorptions show that the coordination of platinum and palladium occurs through the oxygen of the carbonyl group and the heterocyclic nitrogen. Thus both palladium and platinum are hexacoordinated in these complexes with nicotinamide.

The alkaloid, brucine forms 1:1 complexes with Pd(II), Pt(II), Os(IV) and Ir(IV) chlorides. $RhCl_3$ forms a 2:1 complex. The complexes are

TABLE 1—RESULT OF ANALYSES

Metal-nicotinamide complexes Molecular formula	Colour	Decomp. temp. °C	%C	%H	%N	%Cl	Λ_M in ohm^{-1} cm^2 $mole^{-1}$
1. $Pd(C_5H_4N.CONH_2)_2Cl_2$	Yellow	340	34.63 (34.19)*	3.00 (2.87)	13.17 (13.29)	16.31 (16.82)	3.2
2. $Pt(C_5H_4N.CONH_2)_2Cl_2$	Light pink	320	28.00 (28.25)	2.86 (2.37)	10.54 (10.89)	14.5 (13.80)	6.3
Metal-brucine complexes							
1. $Pd(C_{23}H_{26}O_4N_2)Cl_2$	Black	215	48.91 (48.32)	5.01 (4.58)	4.93 (1.90)	11.95 (12.10)	18.1
2. $Pt(C_{23}H_{26}O_4N_2)Cl_2$	Light pink	270	42.80 (41.83)	4.32 (3.96)	4.20 (4.24)	10.91 (10.74)	31.0
3. $Os(C_{23}H_{26}O_4N_2)Cl_4$	Black	above 360	38.00 (38.03)	4.21 (3.61)	3.74 (3.86)	19.96 (19.52)	36.6
4. $Ir(C_{23}H_{26}O_4N_2)Cl_4$	Dirty white	"	35.97 (37.92)	3.88 (3.60)	3.81 (3.85)	20.03 (19.47)	27.6
5. $Rh(C_{23}H_{26}O_4N_2)Cl_3$	Reddish brown	"	34.45 (33.98)	3.80 (3.22)	3.42 (3.45)	25.74 (26.16)	17.0

* Calculated values are given in parentheses

insoluble in water and common organic solvents but slightly soluble in DMF and THF. The molar conductivity measurements carried out in DMSO indicate the non-electrolytic nature of the complexes.

The ir spectrum of brucine shows two bands at 1655 and 1395 cm^{-1}, which are respectively assigned to CO and CN stretching vibrations of the acylazole system[2]. The CO stretching band is lowered by 10 to 20 cm^{-1} in the complexes and it favours the possibility of coordination through oxygen of the carbonyl group. The strong intensity band at 1115 cm^{-1} in the brucine has been assigned to CO stretching of the seven membered cyclic ether[3,4], which shows a slight lowering of frequency in all the complexes except Rh(III) complex where the lowering is quite marked. It is therefore assumed that the second Rh atom coordinates through this oxygen.

On the basis of the ir evidence it may be inferred that Pt(II), Pd(II), Os(IV), Rh(III) and Ir(IV) coordinate through the carbonyl groups of the acylazole ring. The complexes of iridium and rhodium with brucine are found to be diamagnetic.

The thermogram of palladium nicotinamide complex shows a wt. loss of 10.0% at 200° which may be the elimination of $CONH_2$ group (theo. wt. loss is 10.44%). A break in the curve occurs at 30.0% wt. loss at 356°. This may be the elimination of C_5H_4N of the nicotinamide and from which $CONH_2$ was given off (theo. wt. loss = 28.95%). After this, there is a continuous weight loss which may entail the elimination of the second molecule of nicotinamide, sublimation of complex species and the removal of the chloride ions. The weight becomes constant at 81.0% wt. loss at 460° which is more than that calculated for the formation of metallic palladium (74.75%).

The thermogram of platinum brucine complex shows an inflection point at 20.0% wt. loss and 160-200° temperature. This may be due to the elimination of the two OCH_3 groups and the $(CH_2)_3N$ which accounts for 17.86% wt. loss. The maximum weight loss is 73.0% at 380°, which accounts for the formation of metallic platinum (theo. wt. loss = 70.44%). The rhodium complex shows inflection points at 280 and 400° with wt. losses of 52.0% (theo. wt. loss for the formation of 2 $RhCl_3$ 48.47%) and 80.0% (theo. wt. loss for the formation of 2 Rh = 87.34%). These thermograms indicate the removal of two methoxy groups and the $CH_2-CH_2-N-CH_3$ of the aliphatic pyrrocoline ring at low temperatures when nothing else is eliminated. This may mean the non-coordination of the metal ion with this nitrogen in all these complexes as also evidenced by ir spectra.

The electronic spectra of Ir (Brucine) Cl_4 shows bands at 17391, 20833 and 25000 cm^{-1}. This may have a pentacoordinate square pyramidal structure and the first and the last band may be due to $d_{z^2} \leftarrow d_{x^2-y^2}$ and $d_{xz}/d_{yz} \leftarrow d_{x^2-y^2}$ transitions.

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Inorganic Chemistry

STUDIES ON PHOSPHINE AND ARSINE COMPLEXES OF PLATINUM GROUP METALS AND THEIR INTERACTION WITH ACETYLACETONE

ARVIND, M. SAYEED *and* NASEER AHMAD*

Department of Chemistry, Aligarh Muslim University, Aligarh 202 001, India

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Complexes of Ru(III), Rh(III), Pd(II), Ir(IV) and Pt(II) is synthesised by mixing the ethanolic solutions of their chlorides with triphenylphosphine and triphenylarsene and their mixed ligand complexes are prepared by mixing triphenylphosphine or triphenylarsine complexes with acetylacetone. These complexes have been characterised with elemental analyses, m.p. molar-conductance and infrared spectra. The acetylacetone in these complexes is in crystal lattice.

Keywords: Metals; Triphenylphosphine; Triphenylarsene; Complexation; Acetylacetone.

Literature abounds in the triphenylphosphine and triphenylarsine complexes of platinum group metals. Grinberg and Razumova (1945) obtained $Pt(Ph_3P)_2Cl_2$ by the interaction of K_2PtCl_4 with Ph_3P in 1 : 2 molar ratio in ethanolic medium. Vaska and Saloana (1960) obtained $RuCl(Ph_3P)_3$ as yellow crystals by the reaction of $RuCl_3$ with excess triphenylphosphine in boiling $MeOC_2H_4OH$. They also reported the formation of $RuCl_3(PH_3P)_3$ and $RuCl_3(Ph_3As)_3$. Osborn and Wilkinson (1967) refluxed hot ethanolic solutions of $RhCl_3 . 3H_2O$ and Ph_3P and obtained $RhCl(PR_3P)_3$. Recently, the complexes of ruthenium chloride with triphenyl-phosphine, triphenylarsine and acetylacetone have been reported viz., $RuCl(Ph_3P)_3$ acac and $RuCl(Ph_3As)_3$ acac (Natrajan *et al.*, 1977). Very recently, Queiros and Robinson (1978) reported the complexes of β-diketones and presented i.r. evidence to show the presence of 0,0'-coordination. The products of interaction of triphenylphosphine and triphenylarsine with $RuCl_3$, $RhCl_3$, Na_2PdCl_4, Na_2IrCl_6 and Na_2PtCl_6 by the simple process of mixing their ethanolic solutions in cold find little mention in the existing chemical literature although many triphenyl phosphine and triphenylarsine complexes of platinum metals containing hydrido, carbonyl and nitrosyl ligands are being reported in literature using different preparative techniques. The simple triphenylphosphine and triphenylarsine complexes of Ru(III), Rh(III), Pd(II), Ir(IV) and Pt(II) form adducts with acetylacetone which are also being presented in this communication.

**Present Address*: Chemistry Department, Louisiana State University, Baton Rouge, La 70803 (U.S.A.)

EXPERIMENTAL

$RuCl_3 . 3H_2O$, $RhCl_3 . 3H_2O$, Na_2PdCl_4, Na_2IrCl_6 and Na_2PtCl_4 (J. M. Products), triphenylphosphine, triphenylarsine and acetylacetone (B.D.H. products) were used without further purification for the preparation of complexes.

The metal salt solution in ethanol and the solution of the ligand (triphenylphosphine, or triphenylarsine) in the same solvent were mixed with each other and a little warmed to give a crystalline product. It was washed with hexane and dried in vacuo.

The mixed ligand complexes were prepared by mixing the triphenylphosphine or triphenylarsine complexes with acetylacetone.

RESULTS AND DISCUSSION

The elemental analyses for carbon, hydrogen and chlorine give the compositions of the complexes recorded in Table I. The compounds $RuCl_3 . (Ph_3P)$ and $RhCl_3 (Ph_3P)$ are different from the compounds $RuCl_2(Ph_3P)$, $RuCl_2(Ph_3P)_3$ and $RuCl_3 (Ph_3As)_3$ reported by Osborn and Wilkinson (1967). This of course is possible because of the different methods of preparation used by these authors. The products of interaction of Na_2PtCl_4 with triphenylphosphine in ethanol is the same, $PtCl_2 (Ph_3P)_2$, as reported by Grinberg and Razumova but our product is sparingly soluble in common organic solvents and metls at 291 °C whereas theirs is insoluble in common organic solvents and decomposes at 308 °C.

The acetylacetone containing mixed ligand complexes possess the same number of chlorides as present in the simple complexes. The method of preparation of the mixed complexes is such that the oxidation of the metal ions is not possible. The acetylacetone may, therefore, be present as a non-functional molecule. The molar conductances at 10^{-3}M concentration in dimethyl sulphoxide are in the range 65–90 $ohm^{-1}cm^2mole^{-1}$ for 1 : 1 electrolytes (Broomhead & Kane-Maguire, 1967; Greenwood *et al.*, 1968; and Ames & Sears, 1955). All the complexes reported in the table are, therefore, non-electrolytes.

The i.r. bands of triphenylphosphine are retained in its complexes with platinum group metals with no major changes on complex formation. For instance, in dichloro bis (triphenylphosphine) palladium(II), two new bands at 1570(*s*) and 1478(vs) cm^{-1} appear and a medium intensity band of triphenylphosphine at 1278 cm^{-1} disappears. This new band does not appear in the complexes of ruthenium, rhodium, iridium and platinum. The i.r. spectra of the compound of acetylacetone with dichloro-bis (triphenylphosphine) palladium(II) shows all the bands of dichloro-bis(triphenylphosphine) palladium(II) and the acetylacetone and a few more. Very little changes occur when acetylacetone associates with dichloro-bis (triphenylphosphine) palladium(II). The bands occurring at 748, 746, 701, 448, 431 in the simple complex change to 751, 743, 707, 452 and 433 cm^{-1} respectively on interaction with acetylacetone.

The β-diketone chelate complexes have been studied by Lacomte and Morgan (cf. Bellamy, 1958). Lacomte found a strong band between 1562 and 1550 cm^{-1} which he attributes to the carbonyl group weakened by resonance between the

TABLE I

Results of analyses and other characterizing data

S. No.	Compound	Colour	m.p.	%C	%H	%Cl	Molar conductance in $ohm^{-1} cm^2 mole^{-1}$
1.	$RuCl_3 . Ph_3P$	dark grey	220 °C	46.79 (45.90)	3.28 (3.10)	22.3 (22.6)	17.9
2.	$RuCl_2Ph_3P . (acac)_2$	dark grey	210 °C	50.05 (50.17)	4.38 (4.40)	15.5 (15.7)	26.4
3.	$RuCl_3Ph_3As$	dark violet	185 °C	42.16 (42.20)	2.89 (2.92)	20.4 (20.6)	8.5
4.	$RuCl_3 . Ph_3As(acac)_2$	„ „	189 °C	47.01 (47.12)	4.31 (4.34)	14.79 (14.86)	33.5
5.	$RhCl_3 . (Ph_3P)_3$	Yellowish brown	165 °C	58.82 (59.00)	4.05 (4.09)	14.41 (14.46)	9.1
6.	$RhCl_3(Ph_3P) (acac)_2$	greyish brown	170 °C	49.95 (50.09)	4.58 (4.62)	15.58 (15.79)	20.5
7.	$RhCl_3(Ph_3As)_3$	light brown	315 °C	51.95 (52.59)	3.56 (3.61)	12.55 (12.90)	11.1
8.	$RhCl_3(Ph_3As) (acac)_2$	greyish brown	310 °C	45.50 (46.00)	3.91 (4.33)	14.5 (14.8)	6.7
9.	$PdCl_2(Ph_3P)_2$	yellow	263 °C	61.46 (61.50)	4.28 (4.27)	9.08 (10.00)	7.6
10.	$PdCl_2(Ph_3P)_2 (acac)_2$	yellow	255 °C	61.06 (61.20)	4.68 (5.10)	8.00 (7.80)	8.3
11.	$PdCl_2(Ph_3As)_2$	light yellow	246°	54.72 (54.80)	3.74 (3.80)	8.82 (8.90)	6.0
12.	$PdCl_2(Ph_3As)_2 (acac)_2$	dark yellow	250 °C	53.44 (55.30)	3.59 (3.90)	7.30 (7.10)	4.3
13.	$IrCl_4(Ph_3P)_2$	light grey	185 °C	55.05 (56.90)	4.02 (4.01)	12.4 (12.6)	10.2
14.	$IrCl_4(Ph_3P)_2 (acac)$	dark grey	190 °C	57.91 (57.91)	4.29 (4.34)	11.50 (11.60)	14.9
15.	$IrCl_4(Ph_3As)_2$	light yellow	212 °C	51.50 (51.70)	3.58 (3.60)	11.20 (11.10)	19.6
16.	$IrCl_4(Ph_3As)_2 (acac)$	light yellow	160 °C	51.64 (52.30)	3.31 (3.32)	14.60 (14.80)	17.9
17.	$PtCl_2(Ph_3P)_2$	white	291 °C	52.80 (54.62)	3.86 (3.80)	8.08 (8.81)	6.3
18.	$PtCl_2(Ph_3P)_2 (acac)_2$	white	298 °C	53.98 (55.73)	4.42 (4.60)	7.10 (7.06)	6.1
19.	$PtCl_2(Ph_3As)_2$	light grey	292 °C	50.03 (49.18)	3.58 (3.41)	7.40 (8.09)	6.3
20.	$PtCl_2(Ph_3As)_2 (acac)_2$	dark	295 °C	49.72 (50.26)	4.17 (4.00)	7.00 (7.26)	3.9

(Calculated values are given in parentheses)
Ph_3P = triphenylphosphine, Ph_3As = triphenylarsine
acac = acetylacetone.

C—O — M and C = O—M links. In all these substances, there is a band near 1515 cm^{-1} which is attributed to the C = C link (cf. Bellamy, 1958; and Nakamoto, 1963). Nakamoto and Martell (*loc. cit.*) made normal coordinate analysis of the chelate ring of $Cu(acac)_2$ and drew three conclusions : (1) The highest frequency band in the carbonyl region is a C ⋯ C stretching and not a C ⋯ O stretching band as previously concluded, (2) the bands found between 700 and 590 cm^{-1} are sensitive to change in the metal and (3) the newly found bands at 500–400 cm^{-1} are M—O stretching vibrations coupled slightly with the C—CH_3 stretching vibration.

The i.r. spectra of our complexes of triphenylphosphine and triphenylarsine with acetylacetone do not show any new bands in the region of 500–400 cm^{-1}. Hence it is concluded that there is no metal acetylacetone bond in these complexes. The complexes do not show a band near 1515 cm^{-1} which is due to the C = C link and the band at 1550–1562 does not appear in the $PdCl_2(Ph_3As)_2(acac)_2$, $RuCl_3Ph_2P(acac)_2$, $RuCl_3Ph_2As.(acac)_2$, $IrCl_4(Ph_2P)_2(acac)$ and wherever it occurs it is a very weak band. These observations confirm that these complexes have acetylacetone in the crystal lattices.

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ABSTRACT

The diaquo, dipyridyl adducts of tris (heptafluoro octane dione) lanthanide(III), [Ln(Fod)$_3$dipy $2H_2O$], and [M(Fod)$_3$phen] where M=Y, La & Lu have been synthesised and characterised. The Ln(III) in [Ln(Fod)$_3$dipy $2H_2O$] are ten coordinate and retain this higher coordination number even in solution for several days without any trace of dissociation. These seem to have achieved their coordinative saturation and therefore [Pr(Fod)$_3$dipy $2H_2O$] does not act as a Lanthanide Induced Shift reagent. The values of interelectronic and spectral parameters $\bar{\beta}$, $b^{\frac{1}{2}}$ and δ have been computed and the higher values of δ for the Pr, Nd and Er complexes indicate higher covalency. Some ligand field parameters ($b^{\frac{1}{2}}$ and T_λ) and oscillator strengths (P) have been calculated and evidence presented to evince the partaking of f-orbitals in bonding. The higher values of magnetic moments are also a manifestation of higher coordination number.

Mixed Ligand Complexes of Trivalent lanthanide ions with β-diketones and heterocyclic amines.

K. Iftikhar, M. Sayeed and N. Ahmad

Chemistry Department, Aligarh Muslim University,

Aligarh, U.P., INDIA

Introduction: The paramagnetic tris lanthanide(III) chelates[1] of heptafluoro-7,7-dimethyl 4,6-octane dione, (HFod), $Ln(Fod)_3$, have been increasingly used as n.m.r. shift reagents. The chemical property which permits this application is the Lewis acidity which the chelate possesses as a consequence of its coordinative unsaturation. The netural tris chelates dissolve in organic solvents and form labile adducts with a large variety of nucleophilic substrates. Lewis acidity of these chelates also causes two side interactions which may interfere with their usage as nmr shift reagents. Sources of interference are formation of hydrates[2,3] and formation of self associated oligomers.[4-7] McConnell and Robertson[8] derived the relationship for the dipolar shift as:

$$\left(\frac{\Delta H}{H}\right) = -K_p f(\theta,r)\ f(g_{11},g_{\perp})$$

where all the notations have their usual connotations. The dipolar shift depends upon the geometry and magnetic anisotropy of the complex. Thermogravimetric analysis is a useful tool in comparing the relative volatilities and thermal stabilities of the different metal 1,3-diketoenole chelates. Some chelates of acetylacetone are unstable and not volatile, while those of hexafluoroacetyl acetone sublime, albeit in some instances with considerable decomposition.[9]

The absorption spectrum of several of the trivalent lanthanide chelates is a good tool to check the hyper-sensitive bands which vary with environment about lanthanide ions. The intensity of the band in the spectra of lanthanide(III) has been studied both theoretically and experimentally. The theory proposed independently by Judd[10] and Ofelt[11] has been reasonably successful in accounting for the intensity of most of the transitions on the basis of the crystal field induced electric dipole transitions between individual Stark components. The intensity of the normally weak quadrupole transition increases as a result of inhomogeneous field.

Our interest in these newly synthesized adducts of $Ln(Fod)_3$ with 1,10-phenanthroline(phen) and α,α'-dipyridyl(dipy) is to check their ability as potential shift reagents, to investigate the possibility of the involvement of f-electrons in bonding to conclusively prove that these β-diketonates and their adducts do not dissociate in solution to release the heterocyclic amine or one end of the coordinated β-diketone, Hinckley[1] reported dissociation of $Ln(dpm)_3 2py$ to give $Ln(dpm)_3 py + py$ and it was followed by later workers.

Experimental:

Rare earth oxides (Leico Chemicals USA) converted to chlorides, HFod (Pierce Chem. USA), dipy (BDH England) and phen (E. Merck) were used in this study.

Synthesis:

The $Ln(Fod)_3$ chelates were prepared by the method of Sievers et al[2] with a slight modification. The adducts of all the lanthanides (except Ce & Pm) chelates with dipy were prepared by mixing $Ln(Fod)_3$ and dipy in the molar ratio of 1:1 in absolute ethanol. The products thus formed were

crystallized from n-hexane by keeping it in the fridge for 30 days. Good crystals were formed by repeated crystallization. These were dried in vacuo over phosphorus pentoxide. The adducts of $Ln(Fod)_3$ (where Ln is Y, La and Lu) with phen were prepared by mixing $Ln(Fod)_3$ chelates and phen in the molar ratio of 1:1 in absolute ethanol. The pure product was obtained by repeated crystallization from ethanol.

Methods:

A Beckmann DU-2 spectrophotometer was used for obtaining optical spectra in hexane in the range of 10^{-2} to 10^{-3}M at room temperature. The magnetic susceptibility was measured in chloroform using Evans'[12] nuclear magnetic resonance method at the probe temperature. The magnetic susceptibility was also measured using a Faraday Balance. The n.m.r. spectra of the complexes were recorded on Perkine Elmer model 137-B infrared spectrophotometer in nujol mull. The $Gd(Fod)_3dipy\cdot 2H_2O$ complex was subjected to mass spectral analysis at 225°C in $CHCl_3$ on an hp 5985 GC/MS system at Louisiana State University, USA.

RESULTS AND DISCUSSION

The adducts on the basis of their elemental analyses for carbon, hydrogen, nitrogen and metals, molar conductances, i.r., TGA and mass spectra have been assigned the general formula: $[Ln(Fod)_3dipy\cdot 2H_2O]$ and $[Ln(Fod)_3phen]$ (Table 1). The adducts of dipy and phen are very well defined crystalline solids. It is very interesting and striking that even in presence of three bulky ligands, HFod, the lanthanide ions show marvellous avidity for chelating dipy and two water molecules increasing the coordination number of lanthanide ions from six to ten. The adducts are soluble in almost all common organic solvents and insoluble in

water. The molar conductances of these adducts at 10^{-3}M concentration in methanol[13] showed their non-electrolytic behaviour. The phen adducts melt at higher[14] temperature than the dipy ones. Perhaps the rigidly planar phen ligand which in its planarity is like the skeletal β-Ketoenolate anion, permits a more stable crystal packing.

The thermogravimetric analyses of dipy adducts show that the two water molecules present are coordinated to metal ions. In Y, Gd, Ho, Er and Lu complexes the weight loss is from 2.5 to 3.0% (Theoretical weight loss is from 2.90 to 3.09%) in the temperature range of 140°-196°. This strongly indicates that the water present is coordinated (Table 2).

The i.r. spectra of the adducts show a change in the functional group frequencies as compared to their respective chelates. These adducts show a strong band in the region 1560-1580 cm^{-1} and a band between 1600 and 1630 cm^{-1} which are assigned to C=O and C=C stretchings respectively. The bands occurring in the region 370-400 cm^{-1} are attributed to metal-oxygen frequency. The metal oxygen frequencies are lower than those reported in literature.[15] This lowering in νM-O may be due to increase in coordination number. The most diagnostic band suggested for coordinated water lies in the region 800 cm^{-1}-1000 cm^{-1}.[16] On this ground the bands appearing in the range of 932-924 cm^{-1} in the adducts of dipy are an added proof that water is present in the inner coordination sphere which raises the coordination number of Ln from 8 to 10 in dipy adducts. The band in phen at 415 cm^{-1} has shifted to a higher frequency, i.e., 468 cm^{-1}, in the $[La(Fod)_3phen]$. The i.r. shows that both the nitrogens are coordinated to lanthanide[17] ion.

The mass spectra of $Gd(Fod)_3dipy \cdot 2H_2O$ recorded the four heaviest particles with masses 991.5 (0.7% of the most abundant particle, 57.2 amu, taken as 100),

992.6 (0.4%), 993.7 (0.4%) and 997.9 (0.4%). The calculated mass for $Gd(Fod)_3\ 2H_2O$ using average at. wt. for Gd is 994.25. With the limitation of the machine to record only those particles which are capable of accepting a positive charge and having mass nos. 10-1000 amu, it was not possible to detect a particle representing H_2O or $Gd(Fod)_3dipy\cdot 2H_2O$ (at. wt. = 1150.44). The percentage of the particle with amu 156.0 was 36.5 and the at. wt. for dipy is 156.18. Thus it is clear that the two water molecules are more tenaciously attached to Gd than the dipy itself and hence the two water molecules must be coordinated to Gd confirming the coordination no. as 10 for the trivalent lanthanides in $Ln(Fod)_3dipy\cdot 2H_2O$ series.

NMR spectral data for several lanthanide adducts are summarized in Table 3. NMR signals of (Fod) moiety of adducts appear at 0.85-1.11 ppm for t-butyl and at 5.6-5.82 ppm in case of diamagnetic adducts for methine protons as a relatively sharp singlet. Other signals can be assigned to those of the A or B coordinated to the complex.

The signals of coordinated A or B were found to shift remarkably to the lower fields as compared to free A or B. These protons which are shifted to lower fields are subjected to no perturbing influence, other than deshielding expected from electron withdrawing inductive effect of coordination, H-2 are reported to shift to high fields, in case of transition metals, due to metal-non-bonded hydrogen interaction[18] but in our case this interaction is not operative as M-H distance is large. The H-5 in 6, 7 and 8 (Table 3) are shifted to high field. This can probably be related to the conversion of B from a preferred trans configuration when uncomplexed, into a cis configuration when complexed, with attendant loss or reversal of the deshielding effect, specific to H-3, of the magnetic anisotropy of the heteroatom in the attached pyridine

ring, the Van der Waal's repulsion of its lone pair and the electronic dipole moment of the pyridine ring.[19] The t-butyl and methine protons are shifted to high fields in the mixed ligand adducts as compared to their respective chelates.[2] Perhaps this is after withdrawing electron density from A or B, that the Ln^{3+} ion becomes more polarized and transfers some charge via Π-system of diketonate ring and these can be very conveniently accommodated by fluorine (due to its high electronegativity).

The n.m.r. spectra of 1 and 6 show no resonance for free A/B or free β-diketone, no change in signal line width or position is observed even on keeping this solution for two weeks. This clearly proves that both the ends of A as well as diketone remain coordinated in solution and there is no dissociation even at one end of any of the two ligands. The spectra of paramagnetic praseodymium adducts of A or B, showed broad proton signals, giving no high resolution signals due to A or B. This suggests that coordinated base does not dissociate from the praseodymium adduct in solution.

Information concerning electron delocalization in lanthanide complexes may be obtained from n.m.r. studies of paramagnetic species, provided relaxation times are short enough to allow well resolved spectra to be obtained. In the spectra of 4 and 5 the H-2 signal is not observed and the coupling interactions to this nucleus have disappeared, presumably due to paramagnetically enhanced relaxation of this nucleus. The paramagnetic adducts show a greater shift as compared to its diamagnetic analogue since 'g' tensor is anisotropic (i.e., $g_{11} \neq g_{\perp}$) and pseudo-contact interaction is dominant. If 'g' is isotropic this interaction goes to zero. The H-3 and H-5 signals not resolved in diamagnetic adducts, separate in its paramagnetic analogue. The shifts in praseodymium are towards high fields as compared to ytterbium.

In phen adducts of $Tb(Fod)_3$, $Dy(Fod)_3$ and $Ho(Fod)_3$ no resonance is observed either due to phen or diketonate due to high magnetic anisotropy of the central metal ion and the inadequacy of the range of the n.m.r. apparatus.

One of the intents of this study was to examine 4 or 9 and Eu analogue of 9 as potential shift reagents. The [$Pr(Fod)_3$phen] contains coordinated phen leading to a weak complexation with added substrate and a very small shift. In ^1H n.m.r. spectrum of n-butanol two CH_2 groups appear as a single resonance. We find that [$Pr(Fod)_3$phen] added to a CCl_4 solution of n-butanol did not change the spectrum and very small shifts which decrease rapidly with increasing distance of proton from hydroxyl group and CH_2 groups remained as such. The small values of shifts show that it is unsuitable for general use as a shift reagent.

The addition of small amount of ethanol to solutions of 9 or 10 in CCl_4, however, resulted in no change in resonances (even of the hydroxyl proton) of alcohol. The experiment was repeated using 10 and it was found that no change occurs in the spectrum of butanol and in addition the signals of butanol resonate as broad singlets, and coupling disappears. This is due to the bulky nature of the substrate (butanol). The same experiment was repeated using [$Pr(Fod)_3$dipy$\cdot 2H_2O$] which resulted into a slight upfield shift of the entire butanol spectrum (due to change in bulk magnetic susceptibility of the solution) but essentially no alteration in the relative shifts. It is thus apparent from the above discussion that the entropic gain from the bidentate coordination to nitrogen atoms outweighs higher intrinsic affinity of Ln for single oxygen atoms and that these adducts of dipy are totally inefficient as shift reagents.

f-f spectral features:

All the adducts exhibit a very strong spectral absorption at 34.48 kK with a shoulder at 43.48 kK. These bands are attributed to intraligand, $\Pi \rightarrow \Pi^*$ transitions and a band at 29.85 kK due to charge transfer ($n \rightarrow \Pi^*$) transition.[20] A general feature in the spectra of lanthanide ions is a shift of absorption bands towards lower energy on complex formation, i.e., nephelauxetic effect, '$\bar{\beta}$'. This is due to lowering of interelectronic parameters in the complex.[21] If the f orbitals are involved in covalent bond formation with the ligand, the metal wave function can be expressed[22] as

$$\langle \phi_{4f} \mid = (1-b)^{\frac{1}{2}} \langle 4f \mid -b^{\frac{1}{2}} \langle \phi_{ligand} \mid \qquad (1)$$

$b^{\frac{1}{2}}$ measures[23] the amount of 4f orbital mixing, i.e., covalency. Sinha[24] has proposed a δ scale to express the covalency. Both the parameters $b^{\frac{1}{2}}$ and δ are related to nephelauxetic effect, i.e., $\bar{\beta}$. We calculated the values of $\bar{\beta}$, $b^{\frac{1}{2}}$ and δ for the complexes of Pr, Nd and Er (Table 4) as given below:

$$\bar{\beta} = \frac{1}{n} \sum_{n=1}^{n} \nu \text{ complex} / \nu \text{ aquo}$$

$$b^{\frac{1}{2}} = [\tfrac{1}{2}(1-\bar{\beta})]^{\frac{1}{2}}$$

$$\delta\% = \frac{(1-\bar{\beta})}{\bar{\beta}} \cdot 100$$

The broadening in the spectral bands in the adducts of Pr, Nd and Er, as these are highly effected by the surroundings, and the higher values of δ and $b^{\frac{1}{2}}$ indicate greater covalency than that reported earlier.[25]

The f-f transitions[26] are weakly allowed due to some mixing of excited state of opposite parity into ground state (configuration interaction). This

small mixing may be increased on complexation, if the energy of the excited state is lowered. Additional intensity may be gained by the mixing of ligand and metal wave functions due to orbital overlap, so the intensity of the hypersensitive transitions is significantly large. Covalent bond increases the mixing of state of opposite parity required to relax the selection rule for f-f transition, thus increasing their intensity. The intensity of hypersensitive transition changes very much on complex formation whereas that of nonhypersensitive does not, in these complexes. The higher values for hypersensitive transitions are due to eigen perturbation.[27]

The oscillator strength can be computed from an expression,[9,10] derived from a theory in which the ligand field interaction with central ion causes a mixing of higher configuration of opposite parity into the $4f^n$ configuration giving rise to induced electric dipole transitions.

$$P = \sum_{\lambda=2,4,6} T_\lambda \, \nu(\psi^N \Psi_J \,||\, U^\lambda \,||\, \psi^N \Psi'_J)(2J+1)^{-1} \qquad (2)$$

where ν is the energy of transition, $\Psi_J \rightarrow \Psi'_J$, and $U^{(\lambda)}$ is a tensor operator of rank λ and T_λ are ligand field parameters. By substituting experimental[28] oscillator strengths, $P_{Expt.}$ and U^λ values in eq. (2) and using IBM-1130, a set of three parameters, are obtained. These T_λ values have been collected in Table 6. The calculated values of oscillator strength, $P_{calc.}$, using these T_λ values are also collected in Table 5.

In tris (β-diketoenolate) of Pr^{3+} four transitions ($^3H_4 \rightarrow {}^1D_2$; $^3H_4 \rightarrow {}^3P_0$; $^3H_4 \rightarrow {}^3P_1$ and $^3H_4 \rightarrow {}^3P_2$) have been reported[22] but in our adducts only three transitions ($^3H_4 \rightarrow {}^1D_2$; $^3H_4 \rightarrow {}^3P_1$; $^3H_4 \rightarrow {}^3P_2$) are observed. This may be attributed to higher coordination nos., i.e., eight and ten. A good

correlation between $P_{expt.}$ and $P_{calc.}$ for Pr^{3+} adducts, does not strengthen the conclusion of earlier workers[29,30] that the intensity theory of Judd[9] and Ofelt[10] is not applicable to Pr^{3+} complexes. In Nd^{3+} and Er^{3+} adducts also only three transitions are observed, presumably due to the same effect (i.e., bulky nature of β-diketone, heterocyclic amines and increase in coordination number). A remarkable change in P values is seen in case of hypersensitive transition for Nd^{3+} ($^4I_{9/2} \rightarrow {}^2G_{7/2}$, $^4G_{5/2}$) and also for Er^{3+} ($^4I_{15/2} \rightarrow {}^2H_{11/2}$). The lower value of P ($^4I_{15/2} \rightarrow {}^2H_{11/2}$) in [Er(Fod)$_3$phen] is due to splitting of hypersensitive band into three. The higher values of $b^{\frac{1}{2}}$, δ, P and T_λ parameters show that the Ln^{3+} ions in solution are eight and ten coordinate in case of phen and dipy adducts respectively. Generally $b^{\frac{1}{2}}$ value in phen adducts increases from Pr^{3+} to Er^{3+} which indicates that the covalency, i.e., the participation of 4f orbitals, increases as the atomic number increases, which can not be easily explained.

Among the complexes studied, the variation in P and T_λ parameters[31,32] with their sensitivity to their environment and T_λ being in order $T_2>T_4>T_6$, is reported.[33] This order is not strictly followed in our case as all these T_λ parameters are highly sensitive to their environment and there is no remarkable trend.

The magnetic moments, μ_{eff}, of the dipy adducts are higher than those reported[13] for other complexes. This also indicates that 4f orbitals are playing a significant role in bonding. Unfortunately the band calculations are not yet able to describe the $4f^n$ states and their hybridization.[34] Qualitatively speaking, the hybridization should become important because of closeness of d and f states in energy. The hybridization should become stronger for the light rare earths because of large spatial extension[35] of the $4f^n$ shell, a fact which is manifested by the strong K-f scattering.

Square prismatic coordination may be assigned to the octa coordinate adducts of phen of lanthanide chelates where the stereochemistry may be indicative of bonding using f orbitals.[36] For the case of cubical coordination, the A_{2u} irreducible representation of M-L sigma bond is spanned by the metal f_{xyz} orbital, but not by metal s, p or d orbitals. So in the covalent description of the present adducts the ligand may be bonded to the metal by means of hybrid metal orbitals between fd^3sp^3 and f^4d^3s, both of which provide eight equivalent orbitals directed to the cube vertices.

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Table 1. Characterizing Data for [Ln(Fod)$_3$dipy $2H_2O$] and [Ln(Fod)$_3$phen] Complexes.

Complexes	m.p. °C	% Metal	%C	%H	%N	μ_{eff} (B.M.)	$\Lambda_{ohm^{-1}om^2 mole^{-1}}$	Colour
1. La(Fod)$_3$dipy $2H_2O$	101°	11.67 (11.43)	40.04 (39.47)	3.00 (3.29)	2.23 (2.30)	Diamag.	33.93	white
2. Pr(Fod)$_3$dipy $2H_2O$	83°	11.84 (11.58)	39.27 (39.40)	3.23 (3.28)	2.19 (2.29)	4.44	-	green
3. Nd(Fod)$_3$dipy $2H_2O$	80°	11.62 (11.79)	40.00 (39.31)	3.63 (3.28)	2.40 (2.29)	4.67	-	violet
4. Sm(Fod)$_3$dipy $2H_2O$	76°	12.63 (12.25)	39.51 (39.12)	3.12 (3.26)	2.19 (2.28)	3.10 (1.93)*	-	white
5. Eu(Fod)$_3$dipy $2H_2O$	78°	12.76 (12.37)	40.57 (39.06)	3.70 (3.25)	2.30 (2.28)	3.90 (4.20)*	19.70	white
6. Gd(Fod)$_3$dipy $2H_2O$	84°	12.89 (12.72)	39.60 (38.90)	3.50 (3.24)	2.03 (2.27)	9.13	5.3	white
7. Tb(Fod)$_3$dipy $2H_2O$	74°	13.35 (12.86)	40.10 (38.83)	3.49 (3.24)	2.43 (2.27)	10.00 (9.88)*	10.6	dirty white
8. Dy(Fod)$_3$dipy $2H_2O$	85°	13.46 (13.11)	39.10 (38.73)	3.42 (3.23)	2.21 (2.26)	13.31 (13.56)*	9.50	white
9. Ho(Fod)$_3$dipy $2H_2O$	88°	13.86 (13.29)	38.60 (38.65)	3.24 (3.22)	2.30 (2.25)	11.23 (10.80)*	10.70	light yellow
10. Er(Fod)$_3$dipy $2H_2O$	95°	13.03 (13.42)	38.20 (38.59)	3.30 (3.22)	2.46 (2.25)	10.36	9.50	pink
11. Tm(Fod)$_3$dipy $2H_2O$	86°	13.85 (13.56)	39.52 (38.52)	3.51 (3.21)	2.40 (2.24)	7.95	-	white
12. Yb(Fod)$_3$dipy $2H_2O$	93°	14.19 (13.84)	39.63 (38.48)	3.03 (3.20)	2.40 (2.24)	4.79	-	white
13. Lu(Fod)$_3$dipy $2H_2O$	90°	13.90 (13.98)	39.37 (38.34)	3.25 (3.19)	2.23 (2.24)	Diamag.	6.30	white
14. Y(Fod)$_3$dipy $2H_2O$	83°	7.68 (7.63)	41.23 (41.17)	3.38 (3.43)	2.46 (2.40)	Diamag.	5.0	white
15. Y(Fod)$_3$phen	105°	8.36 (8.54)	42.78 (43.67)	3.31 (3.26)	2.54 (2.43)	Diamag.	4.70	white
16. La(Fod)$_3$phen	95°	11.95 (11.54)	42.34 (41.86)	3.09 (3.16)	2.35 (2.33)	Diamag.	8.70	white
17. Lu(Fod)$_3$phen	115°	14.06 (14.11)	41.07 (40.65)	3.26 (3.06)	2.10 (2.26)	Diamag.	5.00	white

Calculated values are in parentheses.

*Magnetic moments in parentheses are in solid state by Faraday Balance.

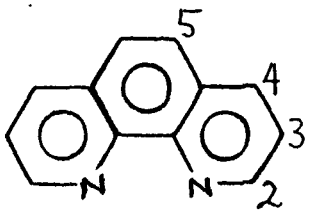
Table 2. [$Ln(Fod)_3dipy\ 2H_2O$] T.G.A. Data.

Complexes	% weight loss for $(H_2O)_2$		
	Temp.	Theo. loss	Exp. loss
$Y(Fod)_3dipy\ 2H_2O$	196°	3.09	3.50
$Gd(Fod)_3dipy\ 2H_2O$	160°	2.90	2.58
$Ho(Fod)_3dipy\ 2H_2O$	140°	2.89	3.00
$Er(Fod)_3dipy\ 2H_2O$	180°	2.89	2.75
$Lu(Fod)_3dipy\ 2H_2O$	190°	2.87	3.00

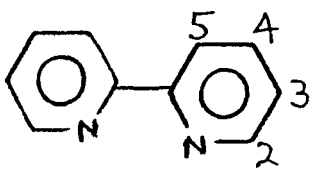
Table 3.

	Compounds	Chemical Shifts[a]			
		H-2	H-4	H-5	H-3
A	- phen	9.16	8.13	7.64	7.75
B	- dipy	8.70	7.80	8.53	7.22
1	$La^{b}(Fod)_3phen^{f}$	9.60	8.29	7.73[e]	
2	$Y^{b}(Fod)_3phen^{f}$	9.58	8.30	7.75[e]	
3	$Lu^{b}(Fod)_3phen^{f}$	9.45	8.26	7.71[e]	
4	$Pr^{b}(Fod)_3phen^{f}$	d	2.54	3.01	-0.65[c]
5	$Yb^{b}(Fod)_3phen^{f}$	d	8.95	14.50	13.60
6	$La^{b}(Fod)_3dipy\cdot 2H_2O$	8.81	7.96	8.10	7.33
7	$Y^{b}(Fod)_3dipy\cdot 2H_2O$	9.44	7.88	7.99	7.47
8	$Lu^{b}(Fod)_3dipy\cdot 2H_2O$	9.35	7.91	8.00	7.46
9	$Pr^{b}(Fod)_3dipy\cdot 2H_2O$	-	-	-	-
10	$Eu^{b}(Fod)_3dipy\cdot 2H_2O$	-	-	-	-

(a) in ppm down field w.r.t. Me_4Si; (b) in CCl_4; (c) in ppm upfield w.r.t. Me_4Si; (d) not observed; (e) Signals H-3 & H-5 quartet; (f) Syntheses of these compounds are reported in J. Inorg. Nucl. Chem. (in press).



A



B

Table 4.

Complexes	$b^{\frac{1}{2}}$	δ	$\bar{\beta}$
$Pr(Fod)_3dipy \cdot 2H_2O$	0.0406	0.3301	0.9967
$Nd(Fod)_3dipy \cdot 2H_2O$	0.0801	1.2076	0.9881
$Er(Fod)_3dipy \cdot 2H_2O$	0.0652	0.8569	0.9915
$Pr(Fod)_3phen$	0.0442	0.3918	0.9961
$Nd(Fod)_3phen$	0.0692	0.9663	0.9904
$Er(Fod)_3phen$	0.0705	1.0051	0.9900

Table 5

Oscillator strength $px10^6$

Complexes	S'L'J'	$P_{Expt.}$	$P_{Calc.}$
$Pr(Fod)_3dipy\ 2H_2O$	$^3P_2$	11.8675	11.8675
	$^3P_1$	7.0740	7.0794
	$^1D_2$	3.7805	3.7805
$Pr(Fod)_3phen$	$^3P_2$	8.0898	8.0897
	$^3P_1$	6.3891	6.3890
	$^1D_2$	4.5384	4.5384
$Nd(Fod)_3dipy\ 2H_2O$	$^4G_{9/2}$	13.2364	13.3424
	$^4G_{5/2}$	59.8545	61.2606
	$^4G_{11/2}$	9.1650	9.1924
$Nd(Fod)_3phen$	$^2D_{3/2}$	2.4024	2.4024
	$^4G_{9/2}$	11.4478	11.4478
	$^2G_{7/2}$	54.0085	54.0097
$Er(Fod)_3dipy\ 2H_2O$	$^4F_{7/2}$	3.9745	4.0468
	$^4F_{9/2}$	3.5250	3.5598
	$^2H_{11/2}$	55.7494	57.5259
$Er(Fod)_3phen$	$^4F_{3/2}$	1.1280	1.1279
	$^4F_{7/2}$	2.5820	2.5820
	$^2H_{11/2}$	22.8737	22.8729

Table 6. T_λ parameters for [Ln(Fod)$_3$phen] & [Ln(Fod)$_3$dipy·2H$_2$O]

	T_2	T_4	T_6
Pr(Fod)$_3$dipy 2H$_2$O	35.8479×10^{-9}	5.8476×10^{-9}	17.9249×10^{-9}
Pr(Fod)$_3$phen	247.2788×10^{-9}	5.3053×10^{-9}	11.8666×10^{-9}
Nd(Fod)$_3$dipy 2H$_2$O	18.8317×10^{-7}	-8.1870×10^{-7}	11.8357×10^{-7}
Nd(Fod)$_3$phen	234.7719×10^{-9}	23.1079×10^{-9}	86.1192×10^{-9}
Er(Fod)$_3$dipy 2H$_2$O	47.80×10^{-9}	2.43×10^{-9}	1.9617×10^{-9}
Er(Fod)$_3$phen	19.9300×10^{-9}	0.15180×10^{-9}	1.5962×10^{-9}

Mixed ligand complexes of trivalent lanthanide ions with β-diketones and heterocyclic amines and their use as possible shift reagents.

BY

Mohd. Sayeed and Naseer Ahmad

Department of Chemistry,

Aligarh Muslim University, Aligarh, INDIA.

ABSTRACT

Sixty new complexes of the trivalent lanthanides (except Pm and Lu) and Yttrium of the general formulae, $Ln(TFAA)_3ophen$, $Ln(TFAA)_3dipy.2H_2O$, $Ln(dpm)_3im$, $Ln(dpm)_3pz$, and $Ln(fod)_3ophen$ where TFAA = trifluoroacetylacetone-H, dpm = 2,2,6,6-tetramethyl 3,5-heptane dione-H, fod = 1,1,1, 2,2,3,3-heptafluoro, 7,7-dimethyl 4,6-octane dione-H, ophen = 1,10-phenanthroline, dipy = 2,2'dipyridyl, im = imidazole and pz = pyrazole, have been synthesised and characterised by their elemental analyses, melting points, molar conductance, magnetic susceptibility, thermogravimetric analysis, and infra red spectral studies. The trivalent lanthanide ions have a coordination number of ten in the series $Ln(TFAA)_3dipy.2H_2O$. Their avidity to enhance their coordination number is so great that even in the presence of three such bulky ligands as heptafluorooctane dione the $Ln(fod)_3$ still coordinates with o-phenanthroline. Hexacoordinated trivalent lanthanides act as LIS reagents but it has been observed that even the eight coordinated and very bulky $Pr(fod)_3ophen$ produces dipolar shifts in the proton resonances of organic moities.

The lanthanide complexes have been studied with various aims, to extend the chemistry of their elements[1], to facilitate the separation of individual members[2-4] and recently for use as pseudo-contact n.m.r. shift reagents[5-9].

The present paper deals with the chelates of trivalent lanthanides with trifluoroacetylacetone,(TFAA), dipivaloylmethane (Hdpm) and 1,1,1, 2,2,3,3-heptafluoro, 7,7-dimethyl, 4,6-octane dione(Hfod) and the mixed ligand complexes of $Ln(TFAA)_3$ with 2,2'dipyridyl(dipy) and o-phenanthroline (o.phen), $Ln(dpm)_3$ with pyrazole and imidazole and $Ln(fod)_3$ with o.phen. These complexes have been characterised by their elemental analyses, melting points, molar conductances, magnetic moments, TGA

and infra red spectra. Some have been scanned for n.m.r. shifts in butan

EXPERIMENTAL:

Materials: TFAA, Hdpm, HFOD , (Pierce Chem. USA); dipy, o.phen (E.Merck) imidazole and pyrazole (Fluka) and rare-earth oxides (Leico Chemicals, converted to chlorides or nitrates, were used in this study.

Preparation of Complexes:

The tris-trifluoroacetylacetonates of the lanthanides[3,10] were mixed with o.phen in the molar ratio of 1:1 in benzene and the crystals obtaine were dissolved in benzene, recrystallised and dried in vacuo. The adducts of dipy with $M(TFAA)_3$ were prepared likewise.

The adducts of tris-dipivaloylmethanates of the lanthanides[1-3] with imidazole were prepared by mixing $Ln(dpm)_3$ and imidazole in the molar rat of 1:1 in carbon tetrachloride. On keeping the solution a crude solid wa deposited. It was recrystallised from carbon tetrachloride thrice to obta the pure product.

The adducts of tris-dipivaloylmethanates of the lanthanides with pyra le were prepared by refluxing a mixture of pyrazole and $Ln(dpm)_3$ in the ar ratio of 1:1 in carbon tetrachloride for about four hours. The crude id obtained was recrystallised from n-hexane thrice, it crystallised as needles.

The mixed ligand complexes of $Ln(fod)_3$ with o.phen were prepared by mixing $Ln(fod)_3$ and o.phen in the molar ratio of 1:1 in absolute ethanol The product thus obtained was recrystallised from absolute ethanol three times. The crystals were dried in vacuo.

The complexes were subjected to microanalysis for carbon, hydrogen an nitrogen and the metal was estimated in some cases by complexometric titrations using EDTA and xylenol orange as indicator. The i.r. and far i.r. spectra of the complexes were taken on a Perkin Elmer model 137B

spectrophotometer in nujol mulls. The molar conductance of 10^{-3}M solutions of the complexes was measured on a Philips PR-9500 conductivity bridge. The magnetic susceptibility was measured at the Chemistry Department, BHU, Varanasi, India on a Faraday balance. Correction for the diamagnetism of the ligand was made. Thermogravimetric analysis was done with a Dupont 950 thermogravimetric analyser at a heating rate of 28°/minute under a nitrogen atmosphere.

$Pr(fod)_3$o phen was added to butanol in varying molar ratios and the nuclear magnetic resonance spectra taken at 31°C on a Varian A-60 n.m.r. machine using TMS as reference. The shifts in the resonances of the CH and the three different CH_2 groups were plotted versus the mole ratio of the $Pr(fod)_3$. o-phen/butanol and straight lines were observed.

DISCUSSION

Trifluoroacetylacetonates and adducts:

The tris-trifluoroacetylacetonate chelates of lanthanides react with dipy and o.phen producing $Ln(TFAA)_3dipy.2H_2O$ and $Ln(TFAA)_3$o.phen enhancing the coordination number of thelanthanide ion from six to eight and ten respectively. This tendency to higher coordination number in the presence of the bulky trifluoroacetylacetone is quite interesting. The complexes of the heavier lanthanides form less readily than those of the lighter ones. This might be because chelates of the larger lanthanide ions are more highly associated than those of the smaller ones.[11] These mixed ligand complexes are quite stable in moist air. They are insoluble in water and soluble in most organic solvents. The molar conductances of these complexes at 10^{-3}M dilution in dimethyl sulphoxide lie between 19.5 and 38.2 ohm^{-1} cm^2mole^{-1}. (The normal range[12] for 1:1 electrolyte is 65-90 $ohm^{-1}cm^2mole^{-1}$). The magnitude of molar conductance is quite

high for non-electrolytes. In another series of β-diketone mixed ligand complexes — tris(dipivaloylmethane) pyrazine lanthanide(III) and tris (dipivaloylmethane)phthalazine the molar conductance in methanol at 10^{-3} concentration were reported in the range of 0.15-0.54 $ohm^{-1}cm^2mole^{-1}$ and 11-32 $ohm^{-1}cm^2mole^{-1}$ respectively [13,14] (range of molar conductances for 1:1 electrolytes[15] 80-115, $ohm^{-1}cm^2mole^{-1}$.)

The melting points of the $Ln(TFAA)_3.2H_2O$ are lower than those of the mixed ligand complexes with o.phen or dipy. The $Ln(TFAA)_32H_2O$ exist as discrete molecules and are not polymeric, hence they have melting points lower than those of the mixed chelates with the bidentate dipy or o.phen. The melting points of neither series show an increase with atomic number of the rare-earth as shown by the tris(dipivaloyl-methane)pyrazine lanthanides(III).[13] But the chelates with o.phen show higher melting points than the corresponding chelates with dipy. In the trifluoroacetylacetone o.phen complexes the melting point increases from cerium to dysprosium (185°C to 214°C) and then decreases to 200°C at ytterbium.

The solubility of these mixed ligand complexes, their modest melting points and eight or higher coordination number, suggests that they are not polymeric.

The magnetic moments of the $Ln(TFAA)_3dipy2H_2O$ are unusually higher than those of the other four series. In attaining a higher coordination no. i.e. 10, there is greater perturbation of the 4f orbitals by the ligand fields[16], leading to greater spatial extension and larger orbital contribution to the magnetic moments.

The $Sm(TFAA)_3$o.phen is diamagnetic whereas $Sm(dpm)_3$, $Sm(dpm)_3$py, $Sm(dpm)_3$dipy, and $Sm(dpm)_3$o.phen are paramagnetic with quite low values of 2.1, 2.1, 2.1 and 2.2 B.M. respectively. Samarium has been shown to

be diamagnetic by Farrel and Wallace[17] in Sm Ni_2. They found the momen of complexes lower than those of the free metal ions and suggested tha it might be due to partial quenching of the orbital angular momentum by crystalline field in the case of Sm Ni_2 and $CeNi_2$. Streitweiser[18] et al have reported magnetic moments of 2.46, 3.47, 3.52, 1.58, 9.6 B.M. for the trivalent Ce, Pr, Nd, Sm, and Tb free ions and values of 1.88, 2.84, 2.98, 1.42 and 9.86 B.M. for the K $Ln(C_8H_8)_2$ complexes respectively. They asserted that the moments correspond closely with the free ion but the values quoted for the Ce[19], Pr, and Nd compounds are lower than the $g(J(J+1))^{1/2}$ values. The observed magnetic moments reported by them are substantially lower than those usually encountered fc Ln^{3+}species. Tsutsui and Ely[20] compared data for their own complexes with the theoretical values of Vleck and Frank[21]and found a good agreement and agreed with Friedman and others[22] that there should not be much deviation from the theoretical values as the 4f orbitals seem to be quite well shielded and should be perturbed only slightly by ligand fields.

The infra red spectra of $Ln(TFAA)_3$, dipy. and $Ln(TFAA)_3$dipy were compared. The infra red spectra of metal acetylacetonates have been studied extensively by many investigators,[23-26] and the following conclusions have been drawn. 1) The highest frequency band (ν_8) in the carbonyl region is a C ⋯ C stretching and not a C ⋯O stretching band as earlier suggested 2) The ν_1 and ν_2 bands found between 700 and 590 cm^{-1} are sensitive to changes in the metal. 3) The bands at 500-400 cm^{-1} are M-O stretching vibrations coupled slightly with the $C-CH_3$ stretching vibrations. Sievers and Bailar[27] have reported that the position of the carbonyl stretching frequency in metal poly aminocarboxylate chelates is influenced by the charge to radius ratio, q/r of the metal ion and that

it occurs at 1590-1615 cm^{-1} when it is less than 3.6 and at 1625-165 cm^{-1} when this ratio is greater than 3.6. The q/r ratio in the lanthanides is less than 3.6. On this basis the various bands in the i.r. spectra of the tris(trifluoroacetylacetone)terbium (taking one examp have been assigned. The 1630 band is due to C ···· C stretching, 153 to C ····O, 1370 to CH_3, 1300 to C=C + C-CH_3, 1195 to C-H, 1140 to -C 1015 and 940 to C-CH_3 and C=C; 855, 781 and 725 to -C-H, 660 to coup Tb-O and ring deformation and 400 cm^{-1} to terbium oxygen stretching. Nag and Chaudhary[28] assigned a band at 425 cm^{-1} to Eu-O in Eu(SDBM) dipy and Eu(SDBM)o.phen where HSDBM stands for 3-mercapto -1, 3-dipho nyl-prop-2-en-1-one or monothiodibenzoyl methane. The Yb-O bands[29] have been reported to lie between 400 and 500 cm^{-1} and recently[30] th Ln-O bands have been mentioned to occur between 402 and 413 cm^{-1}. Th bands occurring at 400, 410, 410 and 410 cm^{-1} in the tris(trifluoroa tylacetonates) of terbium, erbium, thulium and ytterbium can be safe assigned to the metal-oxygen frequency. Clark and Williams[31] observe that an increase in coordination number results in a lowering of M-O bond frequency. According to Nakamoto[32] when some metal acetylaceton form addition complexes with water, pyridine and other bases and the bonding is between the basic atom of the donor molecule and the cent metal ion, a marked shift of the M-O stretching band is anticipated. V-O band (with acetylacetone) is seen at 480 in $VO(acac)_2$ methylamin complexes respectively. The metal oxygen bands in $Ln(TFAA)_3$dipy. 2H$_2$ occur at 395, 400, 390, 393, 400, 398, 398, 400, 389, 410, 403, and 410 cm^{-1} in the complexes of Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb respectively. There is definitely a little lowering in the metal-oxygen band on increase in the coordination number of the meta ions. The $Ln(TFAA)_3$complexes on further complexation with dipy, show

small changes in the bands. There are a few bands for $Ln(TFAA)_3dipy.2$ which are absent in the spectrum of the ligand and also in the Ln(TFA These are at 1695, 1650, 1645, 1648, 1648, 1648, 1650, 1648, 1650, 1 cm^{-1} for Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Tm and Yb and also at 739, 735, 740, 740, 740, 740, 740, 745, 750 and 750 cm^{-1} for the same seque These are due to coordinated water. The metal-nitrogen frequency is a has been a subject of interest. Clark and Williams[33] report that no evidence for ν_{M-L} above 200 cm^{-1} has been found in complexes of neav bidentate nitrogen donor ligands such as dipy and o.phen. The metal-n rogen frequency depends upon the mass of the nitrogen containing liga It decreases as the mass increases.[34-37] According to Ferraro[29] metal-nitrogen bands are very weak and difficult to see. Baranick[38] and oth in 1976 observed that unequivocal assignments of Ln-N frequencies hav been difficult because Ln-halide stretching frequencies may lie in th same region (350-250cm^{-1}) and have greater intensities. Accordingly t assigned a strong band at 299 cm^{-1} with satellites at 305(m), 290(sh 275(sh) cm^{-1} to Yb-N stretching. It is possible that the weak band a ing at 330 cm^{-1} in $Tb(TFAA)_3$ dipy and more or less in the same regio complexes of the other lanthanides may be due to Ln-N stretching.

The adducts of $Ln(TFAA)_3$ with o.phen show only a few peaks of o. in the i.r. There appears to be some increase in the frequencies of vibration of o.phen on complexation as reported earlier.[39,40]

The two water molecules present in $Ln(TFAA)_3dipy.2H_2O$ are coordi to the metal as shown by i.r. and also confirmed by thermogravimetri analysis. In the gadolinium complex, the weight loss starts from 110 and there is loss of 4.7% by 227°C (theoretical wt. loss for two H_2O 4.43%). In the terbium complex there is a weight loss of 4.35%(theo. loss for two H_2O is 4.43%) at 228°C.

Thus in the $Ln(TFAA)_3dipy\ 2H_2O$, the lanthanide(III) ions are ten-

Dipivaloyl methanates and adducts:

The $Ln(dpm)_3$ form adducts with pyrazole and imidazole of general formulae $Ln(dpm)_3pz$ and $Ln(dpm)_3im$. The melting points of the series $Ln(dpm)_3pz$ are lower than those of the corresponding $Ln(TFAA)dipy.2H_2O$ or $Ln(TFAA)_3$ o.phen or even $Ln(dpm)_3im$. In $Ln(dpm)_3im$ the melting point increase from lanthanum to terbium and then decrease to terbium as found for $Ln(TFAA)_3$o.phen. The melting points of the corresponding $Ln(dpm)_3im$ or $Ln(dpm)_3pz$ are lower than those of $Ln(dpm)_3$ o.phen[1]. The planar bidentate o.phen leads to greater stability than the monodentate imidazole or pyrazole. The molar conductances of 10^{-3}M solutions of $Ln(dpm)_3im$ and $Ln(dpm)_3pz$ suggest that the complexes are non-electro. and therefore are seven coordinate (see Table). It is interesting that even in the presence of three molecules of such a bulky coordinating agent as 2,2,6,6-tetramethyl 3,5-heptane dione, a pyrazole or imidazo. molecule coordinates to the lanthanide ions.

The infra red spectra of $Ln(dpm)_3$ $Ln(dpm)_3pz$ and pyrazole were co. pared. ALmost all the bands of pyrazole disappear on coordination. The metal oxygen frequency in $Sm(dpm)_3$ and $Tm(dpm)_3$ occurs at 402 and 40 cm^{-1} respectively. These go up to 410 and 415 cm^{-1} in $Sm(dpm)_3pz$ and $Tm(dpm)_3pz$ respectively. This is an observation in contrast to what been in the trifluoroacetylacetone complexes and many others cited in literature[54] On the formation of an adduct with pyrazole there is an increase in coordination number from six to seven and lowering in metal oxygen bond frequency, as expected.[40] In the i.r. spectra of $Ln(dpm)_3$ im most of the absorption of imidazole do not appear.

Heptafluorobutanoylacetone Complexes:

The $Ln(fod)_3$ form adduct with open (the general formula $Ln(fod)_3$ o.phen. very well defined solids were obtained. Even in the presence of three molecules of such bulky tetramethyl heptane diones, the lanthanide ion

tances of the complexes in methanol at 10^{-3}M dilution suggest that the, are non-electrolytes and are thus eight coordinate (See Table).

The melting points of Ln(fod)$_3$o-phen increase with increase in the atomic number of the lanthanide ion. This is in contrast to the trend observed among the tris-heptafluoro-octane dionates of the lanthanide ions[4] or their monohydrates, Ln(fod)$_3$H$_2$O. The change is most marked for the lighter lanthanides, thereafter the change is small. Sm(fod)$_3$o phen is diamagnetic like the Sm(TFAA)$_3$o·phen.

The infra red spectra of the Ln(fod)$_3$ show a metal-oxygen band at 390 cm^{-1} in Pr(fod)$_3$ and Sm(fod)$_3$ but it splits into two in the adducts with o.phen. The two bands occur at 395 ± 5 cm^{-1} and 410 ± 5 cm^{-1}. Very few bands of o.phen are seen in the Ln(fod)$_3$o-phen.

The paramagnetic shift arises from contact or pseudo-contact (dipolar) interactions, with the dipolar shift predominating in the case of lanthanides as compared to the transition metal ions, because of the limited radial extension of the 4f orbitals. The dipolar shift is limited by the geometry of the complex species, as given by the expressions[42]

$$\frac{\Delta\nu_i}{\nu_0} = -K.f(g)\ F(r.\theta)$$

or simply

$$\frac{\Delta\nu_{dip}}{\nu_0} = -D\left(\frac{3\cos^2\theta-1}{r^3}\right)$$

Where D, θ, r, g have their usual connotations; Shifts have been reported using mostly hexacoordinate lanthanide complexes. Hinckley[5] has used a supposedly eight coordinate complex, Eu(dpm)$_3$2py, but it really acts as the seven coordinate[1], Eu(dpm)$_3$.py. He reported shifts in cholesterol and has found for solutions in CCl_4[43]

$$\text{Eu(dpm)}_3\text{2py} \rightleftharpoons \text{Eu(dpm)}_3\text{py} + \text{py}$$

$$\text{Eu(dpm)}_3\text{py} \rightleftharpoons \text{Eu(dpm)}_3 + \text{py}$$

permitting the coordination of organic functional group containing moities

$$Eu(dpm)_3py + B \rightleftharpoons Eu(dpm)_3py\ B$$

leading to shifts in the proton resonance of B.

Our $Pr(fod)_3$o.phen, having the chelating o.phen has no such possibility of dissociation and decrease of coordination number. The H nmr of this complex does not show any evidence for dissociated o.phen. But $Pr(fod)_3$o.phen still shifts the three methylene and the single methyl resonances of butanol . It is marvellous that in the presence of such bulky ligands as heptafluorooctane dione and o.phen, the $Pr(fod)_3$o phen having a coordination number of eight still attaches the oxygen of the hydroxyl group of butanol, attains coordination no. 9 and produces sizable shifts. The shifts in the CH_2 and CH_3 resonances vary linearly with the concentration of the $Pr(fod)_3$o.phen. Extrapolation to 1:1 molar ratio($Pr(fod)_3$ o.phen: butanol) does not seem possible. The shift is greatest for the proton of the CH_2 nearest the metal ion and least for the methyl protons.

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Table: Elemental analyses and some characterising data. (a)

Complexes of trifluoroacetylacetone and o.phenanthroline:

Name of Complex	%C	%H	%N	%M	m.p. °C	Magnetic moment (μ)(B.M.)	molar conductance $ohm^{-1}cm^2$
Complexes of trifluoroacetylacetone and o-phenanthroline							
1. $Ce(TFAA)_3ophen$	42.08 (41.59)	2.83 (2.56)	3.68 (3.59)		185	2.20	38.1
2. $Pr(TFAA)_3ophen$	41.46 (41.52)	2.87 (2.56)	3.37 (3.58)		205	3.31	34.0
3. $Nd(TFAA)_3ophen$	40.71 (41.37)	2.58 (2.55)	3.64 (3.57)		210	3.48	32.0
4. $Sm(TFAA)_3ophen$	41.02 (41.06)	2.89 (2.53)	3.70 (3.54)		211	diamagnetic	29.8
5. $Eu(TFAA)_3ophen$	40.41 (40.96)	2.41 (2.52)	3.57 (3.53)		214	3.49	34.0
6. $Gd(TFAA)_3ophen$	41.22 (40.69)	2.66 (2.51)	3.59 (3.51)		212-213	7.96	27.2
7. $Tb(TFAA)_3ophen$	39.98 (40.60)	2.62 (2.50)	3.60 (3.50)		212	9.80	26.2
8. $Dy(TFAA)_3ophen$	39.95 (40.44)	2.30 (2.49)	3.42 (3.49)		214	10.90	25.5
9. $Ho(TFAA)_3ophen$	40.22 (40.29)	2.67 (2.48)	3.31 (3.48)		205	10.69	28.9
10. $Er(TFAA)_3ophen$	40.73 (40.19)	2.70 (2.48)	3.30 (3.47)		202	9.88	-
11. $Tm(TFAA)_3ophen$	40.46 (40.07)	2.71 (2.47)	3.70 (3.47)		198-200	7.62	-
12. $Yb(TFAA)_3ophen$	40.16 (39.90)	2.50 (2.46)	3.40 (3.44)		199-200	4.47	-
Complexes of trifluoroacetylacetone and 2,2'dipyridyl:							
1. $Ce(TFAA)_3dipy.2H_2O$	37.49 (37.92)	2.94 (3.03)	3.60 (3.54)	-	178	-	-
2. $Pr(TFAA)_3dipy.2H_2O$	37.49 (37.87)	3.01 (3.03)	3.70 (3.53)	-	182	3.63	23.0
3. $Nd(TFAA)_3dipy.2H_2O$	38.71 (37.73)	2.86 (3.01)	3.52 (3.52)	-	183	3.97	24.9
4. $Sm(TFAA)_3dipy.2H_2O$	36.75 (37.45)	2.83 (2.99)	3.54 (3.49)	-	186	diamagnetic	22.7
5. $Eu(TFAA)_3dipy.2H_2O$	38.72 (37.35)	3.31 (2.92)	3.50 (3.48)	-	187	3.69	21.3
6. $Gd(TFAA)_3dipy.2H_2O$	37.37 (37.12)	3.04 (2.97)	3.50 (3.46)	-	186	8.20	21.3
7. $Tb(TFAA)_3dipy.2H_2O$	36.84 (37.03)	2.93 (2.96)	3.40 (3.45)	-	188	10.88	22.1
8. $Dy(TFAA)_3dipy.2H_2O$	37.19 (36.90)	3.06 (2.95)	3.50 (3.44)	-	184-185	12.04	19.6
9. $Ho(TFAA)_3dipy.2H_2O$	36.67 (36.76)	2.888 (2.94)	3.50 (3.43)	-	184	11.92	22.5
10. $Er(TFAA)_3dipy.2H_2O$	36.35 (36.67)	2.80 (2.93)	3.50 (3.42)	-	175-176	11.30	32.3
11. $Tm(TFAA)_3dipy.2H_2O$	36.39 (36.58)	3.06 (2.92)	3.40 (3.41)	-	178	7.87	36.6
12. $Yb(TFAA)_3dipy.2H_2O$	36.81 (36.40)	2.72 (2.91)	3.30 (3.39)	-	177	4.54	34.0

and imidazole:

	$La(dpm)_3Im.$	57.69 (57.14)	8.06 (8.06)	3.40 (3.70)	- 133	diamagnetic	17.9
.	$Pr(dpm)_3Im.$	55.86 (56.99)	8.26 (8.04)	3.73 (3.69)	- 183-184	3.40	20.0
3.	$Nd(dpm)_3Im.$	55.48 (56.76)	8.16 (8.01)	3.70 (3.67)	- 188-189	3.64	18.70
4.	$Sm(dpm)_3Im.$	55.27 (56.32)	7.75 (7.95)	3.59 (3.65)	- 194	0.50	15.0
5.	$Eu(dpm)_3Im.$	55.34 (56.17)	8.35 (7.93)	3.43 (3.64)	- 192	3.40	13.0
6.	$Gd(dpm)_3Im.$	54.95 (55.81)	7.67 (7.88)	3.70 (3.61)	- 194	8.03	15.
7.	$Tb(dpm)_3Im.$	55.42 (55.67)	7.91 (7.86)	3.66 (3.60)	- 201	9.57	12.0
8.	$Dy(dpm)_3Im.$	54.58 (55.45)	7.81 (7.83)	3.70 (3.59)	- 198	10.62	10.0
9.	$Ho(dpm)_3Im.$	54.74 (55.38)	7.79 (7.82)	3.50 (3.58)	- 196	10.76	10.0
10.	$Er(dpm)_3Im.$	54.76 (55.10)	8.07 (7.78)	3.76 (3.57)	- 196	9.31	9.4
11.	$Tm(dpm)_3Im.$	53.40 (54.98)	7.84 (7.76)	3.70 (3.56)	- 194	7.55	10.2
12.	$Yb(dpm)_3Im.$	53.87 (54.68)	7.38 (7.72)	3.74 (3.54)	- 193	4.26	8.5
13.	Y $(dpm)_3Im.$	58.98 (61.18)	7.54 (7.64)	3.80 (3.96)	- 188	diamagnetic	11.90

Complexes of dipivaloyl methane and pyrazole:

1.	$Pr(dpm)_3pz$	56.82 (56.99)	8.49 (8.04)	- (3.69)	- 150	-	-
2.	$Nd(dpm)_3pz$	55.84 (56.76)	8.27 (8.01)	- (3.67)	- 155	3.69	20.0
3.	$Sm(dpm)_3pz$	56.00 (56.32)	8.49 (7.95)	3.60 (3.65)	- 160	diamagnetic	12.0
4.	$Eu(dpm)_3pz$	55.46 (56.17)	8.29 (7.93)	3.50 (3.64)	- 105	3.40	20.0
5.	$Gd(dpm)_3pz$	54.82 (55.81)	8.01 (7.88)	3.60 (3.61)	- 115	8.40	13.0
6.	$Tb(dpm)_3pz$	- (55.67)	- (7.86)	- (3.60)	- -	-	-
7.	$Dy(dpm)_3pz$	54.58 (55.45)	7.92 (7.83)	3.40 (3.57)	- 118	11.36	15.0
8.	$Ho(dpm)_3pz$	55.45 (55.38)	8.05 (7.82)	3.40 (3.58)	- 130	10.79	11.0
9.	$Er(dpm)_3pz$	53.96 (55.10)	7.54 (7.78)	3.60 (3.57)	- 112	9.37	18.0
10.	$Tm(dpm)_3pz$	55.36 (54.98)	7.57 (7.76)	3.50 (3.56)	- 120	7.38	11.0
11.	$Yb(dpm)_3pz$	55.19 (54.68)	7.90 (7.72)	3.50 (3.54)	- 115	4.35	9.0
12.	Y $(dpm)_3pz$	60.66 (61.18)	9.11 (8.61)	3.90 (3.96)	- 150	diamagnetic	13.0

Complexes of heptafluorodimethyloctane dione and o-phenanthroline:

1.	$Pr(fod)_3ophen$	42.06 (41.85)	3.20 (3.15)	2.03 (2.30)	-	103	2.40	6.1
2.	$Nd(fod)_3ophen$	41.53 (41.66)	3.35 (3.14)	2.12 (2.31)	11.30 11.90	106	3.40	4.4
3.	$Sm(fod)_3ophen$	42.38 (41.48)	3.25 (3.13)	2.52 (2.30)	12.03 12.34	109-110	diamagnetic	4.4
4.	$Eu(fod)_3ophen$	42.26 (41.46)	3.40 (3.12)	2.20 (2.30)	-	112	3.54	-
5.	$Gd(fod)_3ophen$	41.77 (41.24)	3.45 (3.10)	2.17 (2.29)	13.18 12.84	113-114	7,70	6.0
6.	$Tb(fod)_3ophen$	40.83 (41.16)	3.45 (3.10)	2.50 (2.28)	-	113-114	9.60	-
7.	$Dy(fod)_3ophen$	41.60 (41.07)	3.15 (3.09)	2.03 (2.28)	13.9 13.24	114-115	9.6	8.5
8.	$Ho(fod)_3ophen$	41.03 (40.97)	3.81 (3.08)	2.30 (2.27)	-	114	9.3	13.6
9.	$Er(fod)_3ophen$	41.21 (40.90)	3.38 (3.08)	2.30 (2.27)	-	116	9.40	-
10.	$Tm(fod)_3ophen$	41.25 (40.84)	3.84 (3.07)	2.30 (2.26)	-	116-117	7.60	-
11.	$Yb(fod)_3ophen$	40.82 (40.71)	2.74 (3.07)	2.12 (2.26)	-	118-119	4.2	8.45

ABSTRACT

The β-diketoenolates of lanthanide(III) have been known to form adducts with mono and bidentate ligands. The adducts of $Ln(dpm)_3$ and pyrazine have been synthesised and characterised with elemental analyses, molar conductances, i.r., electronic spectra, thermogravimetric analyses and differential thermal analyses. The magnetic moments are in solid state and in solution by n.m.r. technique. Nephelauxetic parameter, $\bar{\beta}$ and covalency parameters ($b^{\frac{1}{2}}$ and δ) have also been calculated and discussed.

Mixed Ligand Complexes of Trivalent Lanthanides with 2,2,6,6-Tetramethyl-3,5-Heptanedione and Piprazine.

K.Iftikhar, M. Sayeed and N. Ahmad

Department of Chemistry,
Aligarh Muslim University, Aligarh

Introduction : Lanthanide complexes have been studied with various aims to extend the chemistry of these elements[1-6] to study their optical spectra for ascertaining the dependence of hypersensitive bands on the environment about the lanthanide ions[7], and to find f-f transitions[8] on complexation and also to use them as n.m.r.shift reagents[9].

The present paper deals with the synthesis and characterization of the mixed ligand complexes of the trivalent lanthanides with 2,2,6,6-tetramethyl-3,5-heptanedione (Hdpm) and piprazine. Nephelauxetic spectral features-nephelauxetic ratio ($\bar{\beta}$), bonding parameter ($b^{1/2}$) and covalency parameter (δ) have been calculated for some of the complexes.[10-12]

Experimental :

Rare earth oxides (Leico Chem. USA) converted to chlorides, Hdpm (Pierce Chem. USA) and piprazine (E. Merk) were used in this study.

Synthesis: The $Ln(dpm)_3$ chelates were prepared by the method of Eisentraut and Sievers.[13] The adducts of all the lanthanides (except Ce & Pm) with piprazine were prepared by mixing $Ln(dpm)_3$ and piprazine

in 1:1 molar ratio in carbontetrachloride. On cooling the solutions a solid was deposited. It was washed with n-hexane and CCl_4 repeatedly and dried in vacuo over P_2O_5.

Methods: The complexes were subjected to microanalyses for carbon, hydrogen and nitrogen and the metal was estimated with complexometric titrations with EDTA using xylenol orange as indicator. The i.r. spectra were recorded on a Perkin-Elmer model 137B spectrophotometer. A Beckmann DU-2 spectrophotometer was used to obtain optical spectra. TGA data were obtained on a manual apparatus with a slow heating rate (6°/minute). DTA studies were carried out at RRL Hyderabad. The magnetic susceptibility was measured on a Faraday balance (in solid state) and by Evans'[14] n.m.r. method (in solution) on a Varian A-60 n.m.r. machine at the probe temperature in DMSO.

Results and Discussion :

The mixed ligand complexes on the basis of their elemental analyses and molar conductances have been assigned the general formula:

$$[Ln(dmp)_3 Piprazine]$$

These adducts are very well defined crystalline solids. They are very stable and can be handled in air without any effect of air or moisture. These are soluble only in warm DMSO. The molar conductance of 10^{-3}M solution in DMSO is 22-28.4 $ohm^{-1}cm^2mole^{-1}$. For 1:1 electrolyte the reported[15] range of molar conductance in DMSO is 65-90 $ohm^{-1}cm^2mole^{-1}$. Thus these adducts are nonelectrolytes in

nature. The adducts melt with decomposition (which is also supported by DTA peaks) and the melting points are higher than those of any mixed ligand complex of trivalent lanthanide and tris(dpm). The high melting points and insolubility, in almost all organic solvents, suggest that these complexes are polymeric in nature. The magnetic moments of these adducts, when plotted against increasing atomic number, show the characteristic unequal double humped curve. Most of the values are from Faraday balance and in a few cases they are measured by n.m.r. technique. The two values in the case of an element are quite close.

The TGA and DTA data for La, Nd, Sm, Eu, Gd, Ho, Dy, and Tm are given in table (2). The partial decomposition occurs for these adducts in the temperature range of 208-255°. The one step DTA "peak" is identified in all cases in this temperature range. The total weight loss in this temperature range is consistent with loss of piprazine. This then means the material left is $Ln(dpm)_3$. This weight loss is also confirmed by TGA. The TGA of these adducts show a weight loss of 10.50-11.00% (theoretical weight loss for piprazine is 10.70-11.04%) in the temperature range of 200-264°C. Our melting points (which are also decomposition points) tally well with the DTA 'peaks'. The melting of these adducts occurring just at or after decomposition point is because of the fact that this decomposition temperature is higher than the melting points of the corresponding chelates! After elimination

of piprazine, only the chelates are left which melt immediately. In the second step of decomposition two molecules of (dpm) are eliminated and one DTA peak is seen in the temperature range of 300-380° and the weight loss in TGA is consistent with the loss of one mole of piprazine and two moles of (dpm). The third mole of (dpm) is eliminated at temperatures above 500°C.

The i.r.spectra of $Ln(dpm)_3$, piprazine and $[Ln(dpm)_3 piprazine]$ is compared. The i.r. spectra in the present study proved to be of limited use in characterizing the compounds since most of the piprazine frequencies lie in the same region as the frequencies of $Ln(dpm)_3$ chelates. However, definite information has been gathered. A sharp band appearing in piprazine at 3205 cm^{-1} (N-H stretching) is shifted to higher frequency and appears in the range of 3280-3268 cm^{-1} as a weak band. Another very strong band appearing at 997 cm^{-1}, in free piprazine, is shifted to lower frequency and appears at 992-968 cm^{-1} in the adducts. These shifts indicate coordination of piprazine. Other bands of piprazine are not seen. On the formation of the adduct with piprazine there is increase in coordination number from six to seven and a lowering in M-O frequency is expected.[16] The M-O frequency in $Sm(dpm)_3$ $Tm(dpm)_3$ appears at 402 and 405 cm^{-1} respectively. These occur in adducts at 355 and 352 cm^{-1}. Thus the bands appearing between 367-350 cm^{-1} are attributed to M-O frequency. In metal polymethylene-carboxylate chelates, the carbonyl frequency is influenced by the charge to radius ratio, q/r, of the metal ion[17] and it occurs at

1590-1615 cm^{-1} when this ratio is less than 3.60 and at 1625-1650 cm^{-1} when q/r is greater than 3.60. The q/r ratio in the lanthanides is less than 3.60. The C=O frequency in $Sm(dpm)_3$ and $Tm(dpm)_3$ appears at 1580 cm^{-1} and 1575 cm^{-1} respectively. But in adducts this is shifted, to higher frequency and appears at 1588 cm^{-1} and 1590 cm^{-1} for the same two metals. The bands in the range of 1570-1590 cm^{-1}, in these adducts, are assigned to C=O frequency.

The electronic spectra of the complexes are recorded in DMSO. The intraligand bands occur in u.v. region and have not been discussed.

A general feature in the spectra of lanthanide ions is a shift of absorption bands towards lower energy on complex formation ie nephelauxetic effect. This is due to lowering of interelectronic repulsion parameter in the complexes.[18] We calculated the nephelauxetic ratio,[10,19] $\bar{\beta}$, and $(1-\beta)$ for the adducts of Pr, Nd, Ho and Er(Table-3). In our complexes the bands are found to shift to lower energy except in the erbium complex in which the bands are slightly shifted to higher energy. This behaviour is quite surprising in view of highly coordinative nature of β-diketone and piprazine. If the 'f' orbitals are involved in covalent bond formation with the ligand the metal wave function is expressed[20] as

$$\langle \phi_{4f} | = (1-b^{\frac{1}{2}}) \langle 4f | - b^{\frac{1}{2}} \langle \phi_{ligand} \qquad (1)$$

where $b^{\frac{1}{2}}$ is the parameter of bonding which measures the amount of 4f-ligand mixing and can be expressed in terms of nephelauxetic ratio, $\bar{\beta}$.[11]

$$b^{\frac{1}{2}} = \left[\frac{1}{2}(1-\bar{\beta})\right]^{\frac{1}{2}} \qquad (2)$$

The positive values of $b^{\frac{1}{2}}$ indicate the covalent bonding. The greater the value of $b^{\frac{1}{2}}$ the greater will be the degree of covalency. Sinha[12] has proposed a δ scale to express the covalency. The δ is also related[12] to nephelauxetic parameter, $\bar{\beta}$. The values of nephelauxetic parameter, $\bar{\beta}$, and covalency parameters ($b^{\frac{1}{2}}$ and δ) are given in table 2. The values of these parameters ($b^{\frac{1}{2}}$ and δ) which are less than one and positive values of $b^{\frac{1}{2}}$ and δ indicate that the nature of bonding between metal and ligand is covalent. We find negative[21] values of δ in case of Er which Sinha[22] interpreted in terms of ionic nature in complexes. This behaviour is quite surprising in view of highly coordinated nature of β-diketone and dipyridine, and calls for further investigations.

A further phenomenon in these spectra is the increase in the intensity of the hypersensitive transitions. The shape of hypersensitive band in Nd^{3+} adduct is similar to that of seven coordinate compounds reported by Karraker[23].

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TABLE -1 Characterizing Data

Complexes	% Metal	% Carbon	% Hydrogen	% Nitrogen	m.p. °C	Colour	Λ_M $Ohm^{-1}cm^2mole^{-1}$	μ_{eff}
$Y(dmp)_3Pip_2$razine	12.31 (12.23)	60.93 (61.33)	9.20 (9.26)	3.81 (3.86)	-	White	28.4	Diama
$La(dpm)_3Pip_2$razine	17.69 (17.95)	57.42 (57.37)	3.50 (3.66)	3.59 (3.62)	260°d	White	25.8	"
$Pr(dpm)_3Pip_2$razine	18.01 (18.17)	57.37 (57.22)	8.58 (8.63)	3.70 (3.61)	260°d	Green	-	3.50 (3.42)
$Nd(dpm)_3Pip_2$razine	18.50 (18.48)	57.02 (57.00)	8.67 (8.60)	3.70 (3.60)	258°d	Violet	-	3.36 (3.3)
$Sm(dpm)_3Pip_2$razine	19.20 (19.15)	56.38 (56.53)	8.49 (8.53)	3.49 (3.57)	260°d	White	20.0	1.83 (2.00)
$Eu(dpm)_3Pip_2$razine	19.33 (19.31)	56.40 (56.42)	8.52 (8.51)	3.50 (3.56)	248°d	White	-	3.56
$Gd(dpm)_3Pip_2$razine	19.79 (19.85)	56.20 (56.04)	8.38 (8.46)	3.55 (3.53)	240-242°d	White	-	7.91 (7.80)
$Tb(dpm)_3Pip_2$razine	19.99 (20.03)	55.81 (55.92)	8.51 (8.44)	3.49 (3.53)	238°d	White	22.5	9.01
$Dy(dpm)_3Pip_2$razine	20.41 (20.38)	55.75 (55.69)	8.49 (8.40)	3.60 (3.51)	233°d	White	-	9.92
$Ho(dpm)_3Pip_2$razine	20.68 (20.63)	55.30 (55.50)	8.40 (8.38)	3.49 (3.50)	225°d	Light yellow	-	10.20
$Er(dpm)_3Pip_2$razine	20.90 (20.82)	55.42 (55.36)	8.42 (8.35)	3.43 (3.49)	219°d	Pink	20.1	9.20 (9.22)
$Tm(dpm)_3Pip_2$razine	21.00 (21.02)	55.30 (55.22)	8.33 (8.33)	3.50 (3.48)	205°d	Light yellow	-	6.93
$Yb(dpm)_3Pip_2$razine	21.37 (21.41)	54.83 (54.95)	8.32 (8.29)	3.51 (3.47)	200°d	White	23.2	4.38 (4.41)
$Lu(dpm)_3Pip_2$razine	21.50 (21.60)	54.97 (54.81)	8.30 (8.27)	3.43 (3.45)	198°d	White	26.3	Diamag

(*) Calculated values are in parentheses, d stands for melting with decomposition, * Values in paranthes from n.m.r.method.

TABLE -2 TGA and DTA Data for some of the Complexes:

Complexes	mp°C	% Loss of Piprazine			% Loss of $(dpm)_2$		
		TGA	DTA peak		TGA		DTA peaks
$La(dpm)_3$Piprazine	260°d	255°	11.00 (11.11)	-	340°	57.00 (58.39)	-
$Nd(dpm)_3$Piprazine	258°d	260°	11.00 (11.04)	258°	346°	56.50 (58.02)	368°
$Sm(dpm)_3$Piprazine	260°d	264°	11.00 (10.95)	-	360°	57.00 (57.10)	-
$Eu(dpm)_3$Piprazine	243°d	250°	10.50 (10.93)	255°	370°	58.00 (57.44)	390°
$Gd(dpm)_3$Piprazine	240-242°d	238°	10.90 (10.86)	239°	370°	60.00 (57.05)	390°
$Dy(dpm)_3$Piprazine	233°d	240°	10.75 (10.78)	-	340°	53.00 (56.67)	-
$Ho(dpm)_3$Piprazine	225°d	230°	10.50 (10.75)	220°	352°	55.00 (56.50)	363°
$Tm(dpm)_3$Piprazine	205°d	200°	11.50 (10.70)	208°	328°	58.50 (56.20)	375°

d melting with decomposition.

Calculated values are in parentheses.

TABLE - 3 Electronic Spectral [illegible] and Their Assignments

Spectral Range cm^{-1}	Energy Level of the band cm^{-1}	β	$(1-\beta)$	$\bar{\beta}$	$b^{1/2}$
		$Pr(dpm)_3$Piprazine			
15625 - 16130	$^1D_2 \leftarrow {}^3H_4$	0.95011	0.04989		
20000 - 20408	$^3P_o \leftarrow {}^3H_4$	0.97359	0.02641	0.97748	0.10611
20833 - 21505	$^3P_1 \leftarrow {}^3H_4$	0.98838	0.01162		
21740 - 23255	$^3P_2 \leftarrow {}^3H_4$	0.99782	0.00218		
		$Nd(dpm)_3$Piprazine			
15870 - 16390	$^2H_{11/2} \leftarrow {}^4I_{9/2}$	0.99320	0.00680		
16390 - 17807	$[{}^4G_{5/2}, {}^2G_{7/2}] \leftarrow {}^4I_{9/2}$	0.97904	0.02096		
18518 - 20000	$^4G_{7/2} \leftarrow {}^4I_{9/2}$	0.98476	0.01524	0.97935	0.10161
20408 - 21276	$^4G_{9/2} \leftarrow {}^4I_{9/2}$	0.98289	0.01711		
21740 - 22727	$^2P_{1/2} \leftarrow {}^4I_{9/2}$	0.95686	0.04314		

Contd.

TABLE -3 (CONTD.)

Spectral Range cm^{-1}	Energy Level of the band cm^{-1}		β	$(1-\beta)$	$\bar{\beta}$	$b^{\frac{1}{2}}$	δ
		[Ho(dpm)$_3$Piprazine]					
17543 - 18867	$^5F_2, ^5S_2 \leftarrow$	$^5I_8$	0.99182	0.00818			
18900 - 20400	$^5F_3 \leftarrow$	$^5I_8$	0.97087	0.02913	0.98783	0.07800	1..
20500 - 23250	$[^5G_6] \leftarrow$	$^5I_8$	0.99448	0.00552			
23250 - 24400	$^5G_5, ^3G_5 \leftarrow$	$^5I_8$	0.99413	0.00587			
		[Er(dpm)$_3$Piprazine]					
11150 - 14285	$^4I_{9/2} \leftarrow$	$^4I_{15/2}$	-	-			
14900 - 15500	$^4F_{9/2} \leftarrow$	$^4I_{15/2}$	1.00879	-0.00879			
17241 - 18200	$^4S_{3/2} \leftarrow$	$^4I_{15/2}$	1.00883	-0.00883			
18200 - 19800	$[^2H_{11/2}], ^4G_{11/2} \leftarrow$	$^4I_{15/2}$	1.00418	-0.00418	1.00921	-	-0.(
20408 - 21050	$^4F_{7/2} \leftarrow$	$^4I_{15/2}$	1.01874	-0.01874			
21050 - 22470	$^4F_{5/2} \leftarrow$	$^4I_{15/2}$	1.00553	-0.00553			

Hypersensitive transitions are enclosed in parentheses.
Assignments are based on reference 1(and references cited therein) and 19.

BIS-ACETYLACETONE BENZIDINE COMPLEXES OF Cr(III), Fe(III), Co(II) AND Ni(II)

Arvind, M. Sayeed, K. Iftikhar* and N. Ahmad**

Department of Chemistry,
Aligarh Muslim University, Aligarh-202001, INDIA

ABSTRACT

Bis-acetylacetone benzidine complexes of Cr(III), Fe(III), Co(II) and Ni(II) are described. The complexes have been given the compositions $[M(ac_2bz)2H_2O]Cl$, where M = Cr(III) and Fe(III) and $M(ac_2bz)$, where M = Co(II) and Ni(II).

INTRODUCTION

Bis-acetylacetone benzidine (ac_2bz) is a tetradentate ligand. We have reported[1] complex of this ligand with Ti(III). We have recently synthesised[2] complexes of this ligand with trivalent lanthanides of general formula $[Ln(ac_2bz)H_2O]Cl$ and have shown that in these complexes lanthanide ions are five coordinate. In continuation to our work here we report complexes of this ligand with Cr(III), Fe(III), Co(II)

** Present Address:

Chemistry Department,
Louisiana State University,
Baton Rouge, La 70803, USA.

and Ni(II). The complexes have been characterized by their elemental analyses, molar conductance, magnetic moments, thermal analyses, IR and electronic spectra.

RESULTS AND DISCUSSION

The bis-acetylacetone benzidine ligand forms complexes with Cr(III), Fe(III), Co(II) and Ni(II) ions which on elemental analyses for carbon, hydrogen, nitrogen and chloride give the composition as reported in Table 1.

The molar conductance range at 10^{-3}M dilution for 1:1 electrolyte in DMSO, is 65-90 $ohm^{-1}cm^{2}mole^{-1}$. As the molar conductance data show (Table 1) the complexes of chromium(III) and iron(III) are 1:1 electrolytes whereas those of cobalt(II) and nickel(II) are non-electrolytes (The measured background conductance of DMSO is $3x10^{-8}ohm^{-1}$). Hence the single chloride is outside the coordination sphere in the chromium and iron complexes. This shows that the ligand in these complexes interacts with the transition metal ion in its enolic form and acts as a bifunctional, tetradentate ligand. This seems to be quite plausible in view of the fact that the complexation with the enolic form leads to more extended π-bonding in comparison to the complex in the keto form.

IR Spectra

The ligand, bis-acetylacetone benzidine[1], shows absorptions at 1625, 1600 and 1550 cm^{-1} which are due to C=O, C=C and C=N stretchings, respectively. The band at 1270 cm^{-1} may be due to the hydroxyl group in hydrogen bonding in the enol form of the ligand. The two strong absorptions at 755 and 800 cm^{-1} are due to the CH deformation of the double bonded carbon in the hydrogen bonded ring.

TABLE I

Analytical Data and Physical Characteristics of the Complexes

Complexes	mp °C	%C	%H	%N	%Cl	$\Lambda_{ohm^{-1}cm^2 mole^{-1}}$	μ_{eff}(BM)	% Yeild
$[Cr(ac_2bz)2H_2O]Cl$ $C_{22}H_{26}ClCrN_2O_4$	220	54.85 (56.23)	5.45 (5.58)	6.01 (5.95)	7.48 (7.54)	60.7	3.67 (3.70)*	65
$[Fe(ac_2bz)2H_2O]Cl$ $C_{22}H_{26}ClFeN_2O_4$	140	56.00 (55.77)	5.24 (5.53)	6.10 (5.91)	7.56 (7.48)	56.7	5.69 (5.65)*	65
$Co(ac_2bz)$ $C_{22}H_{22}CoN_2O_2$	170	64.75 (65.18)	5.40 (5.47)	6.82 (6.91)	-	9.30	4.67 (4.66)*	70
$Ni(ac_2bz)$ $C_{22}H_{22}NiN_2O_2$	180	64.92 (65.22)	5.12 (5.47)	6.87 (6.91)	-	8.50	Diamag.	65

(ac_2bz) = bis-acetylacetone benzidine-H (Enol form-H)

Results in parentheses are theoretical values.

*Values in parentheses are from NMR method.

In the chromium and iron complexes the carbonyl stretching frequency of the ligand shifts to 1610 and 1635 cm^{-1}, respectively. Three bands, at 1520, 1540 and 1570 cm^{-1} in chromium and at 1610, 1560 and 1580cm^{-1} in iron, appear for C=C and C=N stretchings. The band at 1270 cm^{-1} in the ligand disappears in the complex which tallies with the formulation of these complexes with the enolic form of the ligand. The bands at 755 and 800 cm^{-1} appear in the complex but with their position shifted. The bands at 440 and 450 cm^{-1} may be assigned to metal oxygen vibrations for chromium and iron, respectively. The band at 370 cm^{-1} is assigned to the metal nitrogen frequency.

Beside the fundamental mode of vibrations, coordinated water is expected to show other modes of vibration. The bands characteristic of coordinated water are seen near 1012 cm^{-1} and 965 cm^{-1} in $K[Cr(OX)_2(H_2O)_2]\,3H_2O$. A band occuring at 1110 cm^{-1} in both the complexes does not have its equal in the ligand. This band is due to coordinated water.

In the cobalt and nickel complexes, the carbonyl frequency occurs at 1630 cm^{-1} and bands occuring in the C=C and C=N stretching region are 1490, 1540, 1555 and 1610 and 1515, 1550 and 1605 cm^{-1}, respectively. The metal-nitrogen and metal-oxygen absorptions are found at 370 and 415 cm^{-1} in the cobalt complex and at 350 and 375 cm^{-1} in nickel complex.

Thermal Analyses

The thermograms of Cr(III) and Fe(III) complexes show the presence of coordinated water. In the chromium complex a weight loss of about 8.00% occurred (theoretical weight loss for two water is 7.67%) in the temperature range of 160-180°C. The thermogram of the complex showed a

weight loss of 7.5% (theoretical weight loss for two water is 7.61%) in the temperature range of 165-175°. This and IR evidence show that water molecules are present in these complexes which are inside the coordination sphere. All this evidence leads to the formulation of the complexes as:

$$\left[M(C_{22}H_{22}N_2O_2 2H_2O)\right]Cl$$

where M stands for chromium(III) or iron(III).

Electronic Spectra

In the complexes of Ni(II), Co(II), Fe(III) and Cr(III) a very strong band in the region of 28.6-38.5 kK is attributed to the charge transfer transition. The low energy band[5] occurring as a shoulder in Ni(ac_2bz) at 18.55 kK is very weak in intensity due to a large dissymmetry factor and is assigned to the $dxy \rightarrow dx^2\text{-}y^2$ ($^1B_1 \leftarrow {}^1A_1$) transition. The complex is diamagnetic and must, therefore, have square planar structure.

The magnetic moment for Co(ac_2bz) is 4.67 B.M. which is quite comparable with observed values[6] for tetrahedral geometry. The strong absorption at 16.13 and 14.93 kK is mainly due to the spin allowed transition ($^4T_1(P) \leftarrow {}^4A_2$) in tetrahedral symmetry.

The magnetic moment for [Cr(ac_2bz)$2H_2O$]Cl is 3.67 B.M. which is very close to the spin only value for 3 unpaired electrons. The transition at 16.66 kK is assigned to $^4T_2 \leftarrow {}^4A_2$ and at 19.60 kK to $^4T_1 \leftarrow {}^4A_2$. These transitions are indicative of octahedral[7] coordination.

The magnetic moment of 5.69 BM for [Fe(ac_2bz)$2H_2O$]Cl and the absorptions at 16.13 kK ($^2A_2 \leftarrow {}^2T_2$) and 18.18 kK, 17.24 kK ($t_{2g} \leftarrow \pi$) show that Fe(III) has an octahedral environment[7] in this complex.

We find that the shapes of the band for all the complexes described are similar in the solution and in the solid state. This is evidence for the similarity in the environment around the metal ion in both states.

EXPERIMENTAL

All the metal chlorides (BDH), benzidine (E. Merck) and acetylacetone (E. Merck) were used in this study. Acetylacetone was distilled before used.

For the preparation of bis-acetylacetone benzidine, to a well stirred solution of benzidine(0.027 moles) in 200 ml ethanol was added acetylacetone (0.054 moles) in the molar ratio of 1:2. The mixture was heated and vigorously stirred on a hot plate for 4-5 hours when a curdy yellow precipitate separated. It was washed several times with ethanol and dried in vacuo. The crude product was crystallized from chloroform. Repeated crystallization gave shiny yellow crystals(mp 196^{o}).

For the preparation of complexes, the ligand (0.0014 moles) was refluxed in 100 ml methanol for about half an hour and then the metal chloride solution in the same solvent was added (0.0014 moles of metal chloride in 25 ml methanol). The ratio of the ligand and the metal salt was kept 1:1. The reaction mixture was refluxed for about three hours, and then kept on slow heating until a thick layer of the precipitate settled. The supernatant liquid was decanted off and the complex formed was washed with ethanol and chloroform to remove any excess of either metal chloride or the ligand.Finally it was dried in vacuo over P_2O_5.

The complexes were subjected to elemental analyses for carbon, hydrogen and nitrogen. The melting points were measured by the usual method. The molar conductance

of the complexes at 10^{-3}M dilution in DMSO were measured using a Philips Conductivity bridge model PR-9500. The magnetic susceptibility was measured both in solid state with a Faraday balance and in solution by Evans' $^{\delta}$ NMR method on a Varian A-60 NMR machine in DMSO at the probe temperature. The IR spectra of the ligand and the complexes were recorded in nujol mull with a Perkin Elmer IR spectrometer in the range of 4000 cm^{-1} to 200 cm^{-1}. Electronic spectra were recorded on Beckman DU-2 spectrophotometer. The refluctance spectra of the complexes were recorded at Gru Nanak University, Amritsar, in range 200-900 mμ

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ABSTRACT

The β-diketoenolates of lanthanide (III) have been known to form adducts with mono and bidentate ligands. The adducts of $Ln(Fod)_3$ and imidazole have been synthesized and characterised with elemental analyses, molar conductances, i.r., electronic and n.m.r. spectra, thermogravimetric and differential thermal analyses. The electronic spectral parameters $\bar{\beta}$, $b^{\frac{1}{2}}$, δ, P and T_λ have been calculated and discussed. Their possible uses as n.m.r. shift reagents has also been stated.

MIXED LIGAND COMPLEXES OF TRIVALENT LANTHANIDE IONS WITH β-DIKETONE AND IMIDAZOLE

K. Iftikhar, M. Sayeed & N. Ahmad
Department of Chemistry,
Aligarh Muslim University,
Aligarh (U.P) India.

INTRODUCTION:

β-diketoenolates of lanthanides are well known.[1-4] Hinckley[5-6] reported adduct of tris(β-diketoenolate) lanthanide(III) and pyridine and used them as nmr shift reagents. Several mixed ligand complexes of trivalent lanthanides using β-diketones, α,α'-dipyridyl, 1,10-phenanthroline and pyridine have been reported.[7-9] The chelates and mixed ligand adducts of the lanthanide(III) ions are of special interest as potential n.m.r. shift reagents. Their spectral features have also been reported.[10-11] We[12] recently reported eight and ten coordinate mixed ligand complexes of rare earths and studied their n.m.r and f-f spectral features.

The present paper deals with the mixed ligand complexes of all the lanthanides (except Ce and Pm) with heptafluoro-7,7-dimethyl-4,6-octanedione (HFOD) and imidazole(Im). These were synthesized with two main objects. (1) to check their ability as potential n.m.r shift reagents and (2) to study their f-f spectral features. The spectral parameters-oscillator strength (P), nephelauxetic parameter ($\bar{\beta}$) and covalency parameters ($b^{\frac{1}{2}}$ and δ) have been calculated to show the nature of bonding in these complex[10,13-17]

HFOD (Pierce Chem.USA) and Im (Fluka) were used in this study.

The $Ln(Fod)_3$ chelates were prepared by the method of Sievers et al.[3] with a slight modification. The adducts of all the lanthanide chelates (except Ce and Pm) with imidazole were prepared by mixing $Ln(Fod)_3$ and imidazole in the molar ratio of 1:1 in absolute ethanol and refluxing the mixture on a water bath. The products thus formed were washed with n-hexane several times and crystallized in ethanol.

The elemental analyses were done in the microanalytical section of the department. Rare earths were estimated by complexometric titration with EDTA using xylenol orange as indicator.

A Beckmann DU-2 spectrophotometer was used for recording optical spectra in ethanol. I.R. spectra were recorded on a Perkin Elmer model 137-B infrared spectrophotometer. The n.m.r spectra were recorded on a varian A-60 n.m.r machine. The magnetic susceptibility was measured on the same machine using Evans'[18] nuclear magnetic resonance method at the probe temperature. T.G.A are recorded on a manually operating apparatus.

RESULTS AND DISCUSSION:

The adducts on the basis of their elemental analyses for carbon, hydrogen, nitrogen and metal and molar conductances have been assigned the general formula (table 1)

$[Ln(Fod)_3Im]$

All complexes behave as non electrolytes in methanol, as revealed

by their molar conductance data. The adducts are very well defined solids with sharp melting points and are insoluble in water, carbon tetrachloride and n-hexane and soluble in benzene, DMSO, acetone and ethanol.

Selbin et.al[7] for the first time, made use of n.m.r technique for obtaining magnetic susceptibilties of lanthanide complexes. Magnetic moments recorded in table 1,when plotted against the increasing atomic numbers,show the characteristic unequal double humped curve.

The thermograms of the adducts of La, Gd, Tb and Dy showed the same behaviour, as reported for their respective Chelates[3], except in the temperature range of 220-250^{0} in which imidazole is eliminated. The total weight loss in this temperature range is consistant with loss of imidazole (table 3). A sharp DTA peak is identified in most cases in this temperature range. This clearly shows that imidazole is coordinated to the metal ion.

NMR Spectra:

The n.m.r. spectra of the diamagnetic adducts are summarized in table 4. NMR signals of (Fod) moiety of the adducts appear at 0.98 - 1.07 ppm for t-butyl protons and at 5.56 - 5.76 ppm for methine protons as sharp singlets. These signals of t-butyl and methine protons, in adducts, have shifted to higher fields as compared to their respective Chelates[3]. Perhaps this is due to withdrawal of electron density from Im, that the Ln^{3+} ion becomes more polarized and transfers some charge via π -system of diketonate ring, which can be very conveniently accomodated by the

highly electronegative fluorine.

Im is reported[19] to give two n.m.r signals, one for H-2 and the other for(H-4 and H-5)with a relative area of 1:2. But we observed all the three signals for H-2, H-3 and (H-4 and H-5) with relative areas of 1:1:2. The signals of Im show large down field shifts in the adducts. This deshielding effect of Im protons obviously suggests the coordination of Im to metal ion. The signal for H-3 proton is not seen at all.

One of the intents of this study is to examine Im adducts of Pr and Eu as potential shift reagents. Adducts of Pr and Eu added to a solution of n-butanol do not show any significant change in the spectrum of n-butanol. The only change which appears is that the two CH_2 groups, which resonate as a single group, get resolved into two individual signals. Shifts for other protons are very small which is due to the poor solubility of the compound. This should that these adducts are not suitable for general use as n.m.r shift reagents.

Electronic Spectra:

All the adducts show a strong spectral absorption at 47.43 K. and 34.48 K.K. These are attributed to intraligand transition of the type $\pi - \pi^*$ and $n - \pi^*$ respectively[20-21]

itions: A general feature in the spectra of lanthanide ions is a shift of absorption bands towards lower energy on complex formation i.e the nephelauxetic effect. This nephelauxetic shift is related to metal-

ligand covalent bond and is due to lowering of interelectronic repulsion parameter in the complex[15]. If f orbitals are involved in bond formation with the ligand the metal wave function can be expressed as[10]

$$\langle \phi_{4_f} \mid = (1-b)^{\frac{1}{2}} \langle 4f \mid -b^{\frac{1}{2}} \langle \phi_{ligand} \qquad (1)$$

where $b^{\frac{1}{2}}$ is the parameter of bonding which measures the amount of 4f -ligand mixing, and can be expressed in terms of nephelauxetic parameter, $\bar{\beta}$[17]

$$b^{\frac{1}{2}} = [1-\bar{\beta}]^{\frac{1}{2}} \qquad (2)$$

The positive value of $b^{\frac{1}{2}}$ indicates greater covalent bonding between metal and ligand as compared to lanthanide aquo ions. The greater the value of $b^{\frac{1}{2}}$ the greater is the degree of covalency. Sinha has proposed a δ scale to express covalency. δ is also related to $\bar{\beta}$[22], $b^{\frac{1}{2}}$ and δ for the complexes of Pr, Nd, Ho and Er are given in table 5. The $\bar{\beta}$ values, which are less than one and $b^{\frac{1}{2}}$ and δ values which are positive indicate the nature of bonding between metal and ligand is covalent. A negative value of δ shows ionic character in the complexes[23]. The $b^{\frac{1}{2}}$ and δ values in these adducts are in the order Pr > Nd > Ho > Er. This shows that for the same ligand covalency decreases as the atomic number of the lanthanides increases. This is in agreement with the general observation that the nephelauxetic effect is more pronounced in the beginning of the 4f group than for the later members.

Another point of interest in these spectra is the intensity of the f-f- transitions. The transitions known as hyper sensitive

are very much dependant upon the crystal field whereas the other transitions show only slight variation on complex formation[24]. The higher intensity for the hypersensitive transitions is due to eigen perturbation[25].

The oscillator strengths of the most of the intra f-f-transitions in lanthanide(III) complexes can be computed from an expression[13,14] assuming a forced electric dipole mechanism.

$$P = \sum_{\lambda=2,4,6} T_\lambda \Big(\langle f^N \psi_J \| U^{(\lambda)} \| f^{N'} \psi'_{J'} \rangle^2 (2J+1)^{-1} \qquad (3)$$

where all the terms have their usual connotations. By substituting values of experimental oscillator strengths[25], P_{Exp} and $U^{(\lambda)}$ in the eqn.(3) a set of three parameters (T_2, T_4 and T_6) are obtained The values of these parameters are collected in table 6. The P_{Exp} : P_{cal} values are also given in table 7.

The change in oscillator strength in these adducts is evident from the data presented. The normal f-f transition of the complexes are found to be three to five times greater than those of aquo ions where as the hypersensitive band in neodymium is six times greater than the aquo ions. In holmium and erbium the hypersensitive bands are nine and ten times higher as compared to aquo ions.

I.R.Spectra:

The i.r. spectra of the adducts show a change in the functional group frequencies as compared to their respective

chelates[3] (table 2). These adducts show a strong band in the region 1616 - 1648 cm^{-1} and a band in the region 1580 - 1589 cm^{-1} which are assigned to C = C and C = O stretchings respectively. The band occurring in the region 398 - 366 cm^{-1} is attributed to metal-oxygen frequency. The N-H frequency in imidazole is reported[26] to appear as a very broad band (2100 - 3300 cm^{-1}) because of inter-molecular hydrogen bonding. In the adducts this appears as a sharp signal in the region 3200 - 3218 cm^{-1}. The weak band appearing in the region 282 - 290 has been assigned to metal-nitrogen frequency.

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TABLE -1. Characterizing Data for Ln(Fod Complexes

Complexes	%Metal	% Carbon	% Hydrogen	Nitrogen	mp °C	Colour	Λ $Ohm^{-1}cm^2$ $mole^{-1}$	μ_{eff} (BM)
$Y(Fod)_3Im$	8.48 (8.54)	38.29 (38.00)	3.26 (3.26)	2.67 (2.68)	178°	white	10.9	Diamag.
$La(Fod)_3Im$	12.78 (12.73)	36.02 (36.26)	3.31 (3.12)	2.50 (2.57)	208°	white	-	Diamag.
$Pr(Fod)_3Im$	12.79 (12.89)	36.90 (36.20)	3.18 (3.11)	2.49 (2.56)	187°	Green	10.6	3.52
$Nd(Fod)_3Im$	13.08 (13.13)	36.25 (36.10)	2.99 (3.10)	2.62 (2.55)	187-188°	Violet	-	3.82
$Sm(Fod)_3Im$	13.83 (13.63)	35.91 (35.90)	3.15 (3.08)	2.52 (2.54)	185°	white	-	2.22
$Eu(Fod)_3Im$	13.68 (13.76)	35.78 (35.84)	3.03 (3.08)	2.57 (2.53)	185-186°	white	13.2	3.68
$Gd(Fod)_3Im$	14.15 (14.16)	35.52 (35.68)	3.08 (3.06)	2.54 (2.52)	185-186°	white	-	7.80
$Tb(Fod)_3Im$	14.32 (14.30)	35.66 (35.61)	3.10 (3.06)	2.49 (2.52)	158-159°	white	-	9.69
$Dy(Fod)_3Im$	14.50 (14.56)	35.24 (35.50)	2.89 (3.04)	2.50 (2.51)	186°	white	11.8	10.35
$Ho(Fod)_3Im$	14.80 (14.76)	35.46 (35.42)	2.92 (3.04)	2.44 (2.50)	186°	Light yellow	-	10.45
$Er(Fod)_3Im$	15.01 (14.91)	35.30 (35.36)	3.08 (3.03)	2.57 (2.50)	168-170°	Pink	-	9.39
$Tm(Fod)_3Im$	15.02 (15.06)	35.80 (35.30)	3.06 (3.03)	2.61 (2.50)	161°	white	14.1	7.41

TABLE -2. I.R.Frequencies in $Ln(Fod)_3Im$ Complexes

Complexes	ν_{N-H}	$\nu_{C=C}$	$\nu_{C=O}$	ν_{M-O}	ν_{M-N}
$Y(Fod)_3Im$	3200 s	1626 s	1582 w	398 b	290 vw
$La(Fod)_3Im$	3210 s	1616 s	1584 w	376 b	290 vw
$Pr(Fod)_3Im$	3203 s	1648 s	1582 w	375 b	287 vw
$Nd(Fod)_3Im$	3200 s	1640 s	1584 w	377 b	285 vw
$Sn(Fod)_3Im$	3208 s	1624 s	1580 w	367 b	288 vw
$Eu(Fod)_3Im$	3216 s	1621 s	1588 w	366 b	280 vw
$Gd(Fod)_3Im$	3218 s	1630 s	1589 w	375 b	283 vw
$Tb(Fod)_3Im$	3200 s	1626 s	1583 w	382 b	284 vw
$Dy(Fod)_3Im$	3201 s	1630 s	1588 w	374 b	284 vw
$Ho(Fod)_3Im$	3204 s	1630 s	1585 w	377 b	284 vw
$Er(Fod)_3Im$	3220 s	1626 s	1580 w	385 b	282 vw
$Tm(Fod)_3Im$	3208 s	1625 s	1580 w	395 b	280 vw
$Yb(Fod)_3Im$	3214 s	1624 s	1584 w	376 b	289 vw

s = strong, w = weak, b = broad & vw very weak

TABLE - 3: TGA Data For Some of the Complexes

COMPLEXES	Temperature ^{o}C	% weight loss for imidazole
$La(Fod)_3$ Im	220	6.50 (6.22)
$Gd(Fod)_3$ Im	240	5.50 (6.12)
$Tb(Fod)_3$ Im	246	6.00 (6.06)
$Dy(Fod)_3$ Im	225	6.00 (6.10)

Theoretical weight loss is in parentheses

TABLE-4: Nuclear Magnetic Resonance Spectra for $Ln(Fod)_3Im$ Complexes[a]

Ln	L	Signals due to Imidazole			Signals due to ketoenolate	
		H-3	H-2	(H-4 & H-5)	CH	Bu^t
-	Imidazole[b]	12.53	7.78	7.18	-	-
La	Imidazole	c	8.35	7.30	5.76	1.07
y	Imidazole	c	8.25	7.30	5.70	1.03
Lu	Imidazole	c	8.37	7.37	5.65	0.98

[a] Obtained in dimethyl sulphoxide at probe temperature. Peak positions are given in ppm down field from Me_4Si.

[b] Obtained in deuterated chloroform.

[c] not observed.

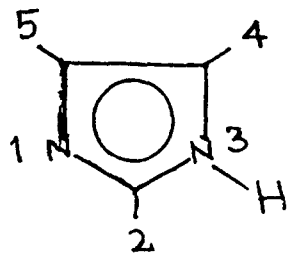

TABLE -5: Covalency Parameters for ($Ln(Fod)_3Im$) Complexes

Complexes	$\bar{\beta}$	$b^{\frac{1}{2}}$	δ
$Pr(Fod)_3Im$	0.97977	0.10058	2.06496
$Nd(Fod)_3Im$	0.98231	0.09406	1.80145
$Ho(Fod)_3Im$	0.98737	0.07945	1.27853
$Er(Fod)_3Im$	0.99482	0.05093	0.52151

TABLE -6: T_λ Parameters for $Ln(Fod)_3Im$ Complexes

$T_\lambda \times 10^9$

Complexes	T_2	T_4	T_6
$Pr(Fod)_3Im$	64.74498	2.55084	28.41594
$Nd(Fod)_3Im$	19.65370	6.68132	26.19470
$Ho(Fod)_3Im$	14.38708	1.62136	3. 91197
$Er(Fod)_3Im$	24.33770	1.37202	4.85637

TABLE - 7. Oscillator Strengths, P x 10^{-6}

Complexas	$\overline{\lfloor}$'S'L'J'$\rfloor$	P_{Exp}	P_{Cal}
$Pr(Fod)_3Im$	$^1D_2$	5.44946	5.44944
	^3P_o	5.13355	7.32197
	$^3P_1$	4.40301	3.08814
	$^3P_2$	18.12540	18.12735
$Nd(Fod)_3Im$	$[^2G_{7/2}$ $^4G_{5/2}]$	61.27090	59.47819
	$^4G_{7/2}$ $^4G_{9/2}$	8.44000	6.96878
	$^2K_{15/2}$	0.53300	0.53[illegible]
	$^2P_{1/2}$	0.60418	0.60
$Ho(Fod)_3Im$	$^5F_4$ $^5F_3$	7.74090	7.74[illegible]
	$[^5G_6]$	66.38190	65.6[illegible]27
	$(^5G, ^3G)_5$	1.68712	1.587[illegible]4
$Er(Fod)_3Im$	$^4F_{9/2}$	6.91253	4.052[illegible]6
	$^4S_{3/2}$	2.68372	3.93153
	$[^2H_{11/2}]$	26.36179	17.73814
	$^4F_{7/2}$	2.08797	7.00369
	$^4F_{5/2}$	4.30034	3.30533
	$^4G_{11/2}$	19.82243	31.84934

Hypersensitive transitions are enclosed in parantheses.

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LANTHANIDE SHIFT REAGENTS; SYNTHESIS AND SPECTRAL STUDIES

Khalid Iftikhar, Mohd. Sayeed and N. Ahmad*
Department of Chemistry,
Aligarh Muslim University, Aligarh-202001 (U.P) INDIA.

ABSTRACT

The seven coordinate adducts of $Ln(Fod)_3$ chelates are described. The NMR spectra of diamagnetic and paramagnetic adducts have been discussed. The Europium, Praseodymium and Ytterbium adducts have been scanned as potential shift reagents and these seven coordinate adducts produce large dipolar shifts in the proton magnetic resonances of organic moieties. The dipolar shift produced by $Eu(Fod)_3P_2$ in the spectrum of benzyl alcohol is different from that reported. Some interelectronic and spectral parameters (β, $b^{\frac{1}{2}}$ and δ) have been calculated. Ligand field parameter (T_λ) and oscillator strengths have been computed and discussed.

Introduction: NMR spectra may usually be obtained from the complexes of paramagnetic lanthanide ions with organic ligands.[1,2] Such spectra commonly show paramagnetic shifts, mainly of dipolar (pseudo-contact) origin. This principle has been applied by Hinckley[3] to weak association between

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* Present address: Chemistry Department,
Louisiana State University
Baton Rouge, La 70803 U.S.A.

tris(dipivaloylmethanato) Europium(III) and cholestrol (the complex being used as its bis-pyridine adduct). Further investigations have established that (1) $Eu(dpm)_3$, dpm=2,2,6,6 tetramethyl-3,5-heptanedione, itself (i.e., without the pyridine molecules appended) is even better than the pyridine adduct[4] (pyridine tends to block coordination of substrate) (2) the analogous praseodymium compound, $Pr(dpm)_3$, induces NMR shifts of opposite sign[5] and also much larger than those reported for $Eu(dpm)_3$. Selbin et.al.[6] reported a series of analogous lanthanide complexes with the same bulky β-ketoenol and their mixed ligand complexes with mono and bidentate ligands. Ahmad et al.[7] studied the temperature dependant shifts. It has been pointed[8] out that the mixed ligand adducts $Eu(dpm)_3$dipy and $Eu(dpm)_3$o.phen (dipy = 2,2'dipyridyl and O.phen = 1,10-phenanthroline) are inefficient in producing shifts. We[9] have shown that our eight coordinate adduct, $Pr(fod)_3$O.phen (fod = 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione) produces dipolar shifts in the proton resonance of n-butanol and also it does not dissociate in solution as reported by Hinckley[3], for eight coordinate complex. Recently[10-12] we have synthesised seven, eight and ten coordinate complexes of lanthanides and studied their electro spectra. During these investigations it has been found that as the coordination number increases the number of bands decrease and also the intensity of the hypersensitive bands increases.

The present paper deals with the synthesis and characterization of seven coordinate adducts of $Ln(Fod)_3$ chelates with pyrazole (P_z) and possible use of their Europium, Praseodymium and Ytterbium adducts as lanthanide induced shift reagents. Covalency parameters[13-16] ($\bar{\beta}$ and δ), bonding parameter ($b^{\frac{1}{2}}$) have been calculated and discussed. Oscillator strength (P) have also been computed for some of the complexes.[17-19]

EXPERIMENTAL:

Rare earth oxides (Leico chem., USA) were converted to corresponding chlorides. HFDD (Pierce Chem. USA), Pyrazole, P_z, (Fluka) and Xylenolorange (BDH England) were used in this study.

Synthesis: $Ln(Fod)_3$ chelates were synthesised by the method of Sievers et al.[20] with a slight modification. The adducts of all the lanthanides with pyrazole were prepared as follows:

The pyrazole was refluxed in ethanol for one hour, the solution of $Ln(Fod)_3$ chelates (in 1:1 ratio) was mixed with it. Finally the mixture was refluxed for four hours on a water bath. Then the solvent of the resulting mixture was evaporated on a hot plate. The product thus formed was crystallised from n-hexane by keeping it in fridge for 30 days. Good crystals were obtained by repeated crystallization. Finally these were dried in vacuo over P_2O_5 for several days.

Methods: Carbon, hydrogen and nitrogen contents of the complexes were estimated by microanalyses while the metals were estimated by complexometric titrations with EDTA using xylenol orange as the indicator. The IR spectra were recorded on a Perkin-Elmer model 137 B spectrophotometer in the range 4000-200 cm^{-1}. A Beckman DU-2 spectrophotometer was used to obtain the optical spectra. The NMR spectra were recorded on a varian A-60 NMR machine in carbon tetrachloride. The magnetic susceptibility was measured by Evans'[21] NMR method in methanol as well as in chloroform at probe temperature. TGA and DTA studies were carried out at RRL Hyderbad, India.

CALCULATIONS:

On complexation radial integrals of the valence orbital of the metal ion decrease . This phenomenon is known[13] as nephelauxetic effect and may be regarded as a measure of the covalency in a complex. Nephelauxetic ratio, $\bar{\beta}$, can be calculated from the relation[13]

$$\bar{\beta} = \frac{1}{n} \sum_{n=1} \nu^{i}_{comp} / \nu_{aq} \qquad (1)$$

If the f orbitals are involved in covalent bond formation with the ligand the metal wave function can be expressed[14] as

$$\langle \psi_{4f} | = (1-b)^{\frac{1}{2}} \langle 4f | - \underline{b}^{\frac{1}{2}} \langle \psi_{ligand} | \qquad (2)$$

where $\underline{b}^{\frac{1}{2}}$ measures the amount of 4f -ligand mixing and is

calculated from the relation[15]

$$\underline{b}^{\frac{1}{2}} = \left[\tfrac{1}{2}\,(1-\bar{\beta})\right]^{\frac{1}{2}} \qquad (3)$$

The positive and negative values of $\underline{b}^{\frac{1}{2}}$ for a complex correspond to covalent and ionic characters respectively.

Sinha's covalency parameter[16], δ, is calculated from the relation

$$\delta = \left[\frac{1-\bar{\beta}}{\bar{\beta}}\right] 100 \qquad (4)$$

The experimental values of the oscillator strength (P_{exp}) of the absorption bands are calculated by performing Gaussian curve analyses of the curves and using the equation[1

$$P_{exp} = 4.31 \times 10^{-9} \left[\frac{9n}{(n^2+2)^2}\right] \int \epsilon\,(\bar{\nu})\, d\bar{\nu} \qquad (5)$$

where n is the refractive index of the medium, ϵ is the molar extinction coefficient and $\bar{\nu}$ is the energy of the transition in wave number.

The Oscillator strengths (P_{Theo}) can be computed from an equation[17,18] derived from a theory in which the ligand field interaction with central ion causes a mixing of higher configuration of opposite parity into the $4\underline{f}^n$ configuration giving rise to induced electric dipole transions.

$$P = \sum_{\lambda=2,4,6} T_\lambda\, \bar{\nu}\, (\psi_J \| U^{(\lambda)} \| \psi_J')^2\, (2J+1)^{-1} \qquad (6)$$

where ν is the energy of transition, $\psi_J \longrightarrow \psi_{J'}$ and $U^{(\lambda)}$ is the unit tensor operator connecting the initial and final states *viz* three phenomenological parameters T_λ (λ=2,4 and 6). The three T_λ parameters are related to the radial part of the $4f^n$ wave functions, the wave functions of the perturbing configurations, the refractive index of the medium and the ligand field parameters characterizing the environment of the ion. The three quantities, T_λ, can be treated as the parameters to be determined from the experimental oscillator strengths.

RESULTS AND DISCUSSION

These adducts are well defined crystalline solids with sharp melting points. The melting points of pyrazole adducts are lower than those of imidazole adducts.[12] These are soluble in all organic solvents and are air stable. The molar conductance of these complexes in methanol (Table 1) showed their non-electrolytic behaviour.[22]

IR Spectra: The IR spectra of these adducts show the presence of coordinated pyrazole. The N-H frequency in pyrazole ligand appears as a broad band (2300-3500 cm^{-1}), but because of intermolecular hydrogen bonding, it appears as a sharp band in the region 3000-2940 cm^{-1}, in the adducts. The weak band found between 305 and 290 cm^{-1} in these adducts has been assigned to M-N frequency. We have found the M-N frequency in the

same region (282-290 cm^{-1}) for imidazole adducts[12] of $Ln(Fod)_3$ chelates. The metal-oxygen frequency in $Pr(Fod)_3$ and $Sm(Fod)_3$ occurs at 390 cm^{-1}. These go up to 454 cm^{-1} and 450 cm^{-1} in the corresponding adducts. Thus the bands appearing between 445 & 460 cm^{-1} have been assigned to metal-oxygen frequency in these adducts. This is an observation in contrast to what is seen in imidazole[12] adducts.

The thermograms of the adducts of La, Eu, Gd, Tm and Yb showed the same behaviour as reported for their respective chelates[20], except in the temperature range of 200-220°C in which pyrazole is eliminated. The total weight loss is consistent with the loss of pyrazole in this temperature range (Table-2). One sharp DTA peak is identified in all cases.

Thus these adducts on the basis of their elemental analyses for carbon, hydrogen, nitrogen and metals, molar conductance (Table-1), IR spectral and thermal studies have been assigned the general formula,

$$[\ Ln(Fod)_3P_z\ ]$$

The magnetic moments (Table-1) of these adducts, when plotted against their increasing atomic number, showed the same characteristic double humped curve.

NMR Spectra: The NMR spectral data are summarized in table-3. NMR signals of Fod moiety of the adducts appear at

1.05 - 1.15 ppm for t-butyl protons and at 5.95 - 6.11 ppm for methine protons as sharp siglet (for diamagnetic adducts). It has been found that the signals due to t-butyl and methine protons have been shifted to higher fields as compared to their respective chelates.[20] Perhaps it is due to withdrawal of electron density from pyrazole, that the Ln^{3+} ions become more polarized and transfer some charge to diketonate ring, which can be very conveniently accommodated by the highly electronegative fluorine. Other signals can be assigned to those of the coordinated pyrazole.

Pyrazole is reported[23] to give two signals (one for H-4 and another for H-3 and H-5) with relative areasof 1:2. But we found all the three signals [for H-2, H-4 and (H-3 and H-5) with relative areas of 1:1:2. The signals of the coordinated pyrazole are found to shift to the lower fields, except in the case of lanthanum in which the signals are slightly shifted to higher fields. This deshielding effect of pyrazole protons obviously suggests the coordination of pyrazole to metal ion.

Information concerning electron delocalization in lanthanide complexes may be obtained from NMR studies of paramagnetic species, provided relaxation times are short enough to allow well-resolved spectra to be obtained. Paramagnetic lanthanide complexes whose spectra have been recorded are few.[1,8] In the spectra of $Pr(Fod)_3P_z$ and $Yb(Fod)_3P_z$ the methine signal is not seen but the proton resonances of pyrazole show large chemical shiftsas compared

to their diamagnetic analogue. These shifts are due to pseudo-contact (dipolar) interaction as g tensor is anisotropic. If g is isotropic this interaction goes to zero. The dipolar shift is limited by the geometry of the complex species, as given by the expression[24]

$$\frac{\Delta\nu}{\nu_0} = - K_p f(\theta, r) f(g_{\parallel}, g_{\perp})$$

or simply

$$\frac{\Delta\nu}{\nu_0} = - D \left(\frac{3\cos^2\theta - 1}{r^3} \right)$$

where all notations have their usual connotations.

One of the intents of this study was to examine Pr, Eu and Yb adducts as potential shift reagents. $Eu(Fod)_3P_2$ added to a solution of n-butanol show large chemical shifts (Figure-I). The two methylene protons which resonate as a singlet get resolved into two individual signals. The substrate associates with the complex at the hydroxyl group and the induced shifts decrease rapidly with increasing distance of the protons from the hydroxyl group. When Pr(Fod)$_3$ was used, it induced the butanol spectrum to become first order and all peaks greatly shifted to high field (Figure-3). On addition of $Yb(Fod)_3P_2$, the spectrum is amenable to a first order analysis and the magnitude of the induced shift is large, than the Eu adduct, but with a little broadening and the coupling interactions of the nuclei having disappeared.

This little broadening is due to long relaxation time of Yb(III ion as compared to Europium (III). In the above examples, the shifts of the hydroxyl protons are of course extremely large and have not been recorded, (See tables 4-6).

In the normal H¹NMR spectrum of benzyl alcohol (CCl_4 solution) the aromatic protons resonate as a sharp singlet. Sanders and Williams[4] studied NMR spectrum of benzyl alcohol using $Eu(dpm)_3$ and reported that the signals appear in order CH_2 , O-protons, m-protons and then p-proton (all lower field to TMS). Our studies gave a different result. $Eu(Fod)_3$ when added to a CCl_4 solution of benzyl alcohol resolved all the ring protons (Figure-2) but in a different manner as reported[4]. The CH_2 protons appear at the lowest field as a sharp singlet, the next resonance is due to o-proton and the m-protons appear at the last (all lower field to TMS). When $Pr(Fod)_3$ is used only CH_2 signal appears at higher field toTMS the other signals lie within the TMS envelope. The CH_2 proton resonance shows that the angle between the principal axis and line joining the paramagnetic ion and the proton in question is greater than 54.7° or 125.3°.

The NMR spectra of these adducts show no resonance for free pyrazole. Even on keeping the solutions for several days no change in signal line width or position is seen. This shows that coordinated pyrazole does not dissociate in

solution as reported by Hinckley[3] for pyridine.

Electronic Spectra:

The electronic spectra of the complexes are recorded in ethanol. The intraligand transitions occur in u.v. region and have not been discussed. The sharp line like f - f transitions originating with in the $4f^n$ configuration of lanthanide (III) ions are affected by the influence of the ligands on complexation. The shift of absorption bands to lower wave numbers (nephelauxetic effect) is usually of the order of a few percent[13] and is caused by a decrease ~~by a decrease~~ in inter-electronic repulsion parameter in the complexes.[25] A general red shift of the f-f transitions would be observed for these complexes as compared to the corresponding aquo-ions. The $\bar{\beta}$ values for these complexes are presented in table 7. The $\bar{\beta}$ values which are less than one shows covalent nature of bonding between the metal and the ligand. The $\bar{\beta}$ value of Nd(III) complex is higher than the Pr(III) complex but it is lower for Er(III) complex as compared to Nd(III) complex. This is in contrast to the general observation that the nephelauxeti effect is more pronounced in the beginning of the 4f group than in the latter members. The bonding parameter, $b^{\frac{1}{2}}$ and Sinha's covalency parameter, δ are positive for these comple indicating covalent bonding (Table 7). The greater the value of $b^{\frac{1}{2}}$ and δ the greater will be the degree of covalency. The $b^{\frac{1}{2}}$ and δ values of Nd(III) complex are less than those for Pr(III)

complex showing decrease of covalency with increase of atomic number. The higher values of $\underline{b^{\frac{1}{2}}}$ and δ for Er(III) complex than Nd(III) complex are surprising in view of the general observation and the trend observed in case of $Ln(Fod)_3Im$ (Im= Imidazole) complexes.[12] The $Ln(Fod)_3P_x$ complexes are less covalent as compared to the corresponding $Ln(Fod)_3Im$[12] complexes since values of $\underline{b^{\frac{1}{2}}}$, δ and $\overline{\beta}$ are lower in the former case than in the latter.

Another point of interest in these spectra are the intensities of the f-f transitions. Experimentally hypersensitivity refers to transitions having oscillator strengths which show a relatively large variability in oscillator strengths as the environment about the lanthanide ion is changed. The large variability in oscillator strengths for the hypersensitive transitions is due to eigen perturbation.[19] Hypersensitivity can also be discussed from the theoretical point of view of Judd-Ofelt. According to this theory hypersensitivity is intimately associated with T2 parameter of equation (6). Consequently only those transitions having relatively large values of $U^{(2)}$ matrix element should be called hypersensitive. Judd[26] has suggested that hypersensitivity may be due to asymmetry of the crystal fields. Henrie[27] has shown that T_4 and T_6 appear to be primarily influenced by the symmetry of the complexes whereas T_2 seems to be correlated with the basicity of the ligand.

The oscillator strengths are listed in table 9 and hypersensitive transitions classified by previous workers[27]

The oscillator strength of the hypersensitive transitions is related to the degree of covalency. As the covalency in the complex increases the oscillator strength of the hypersensitive transition exhibits a corresponding increase. The oscillator strengths of the hypersensitive transitions of pyrazole complexes have lower values as compared to the corresponding imidazole complexes[12] since imidazole is more basic than pyrazole.

In the last we can say that pyrazole complexes, though less covalent, have superiority over imidazole complexes[12] since they can be used as potential shift reagents.

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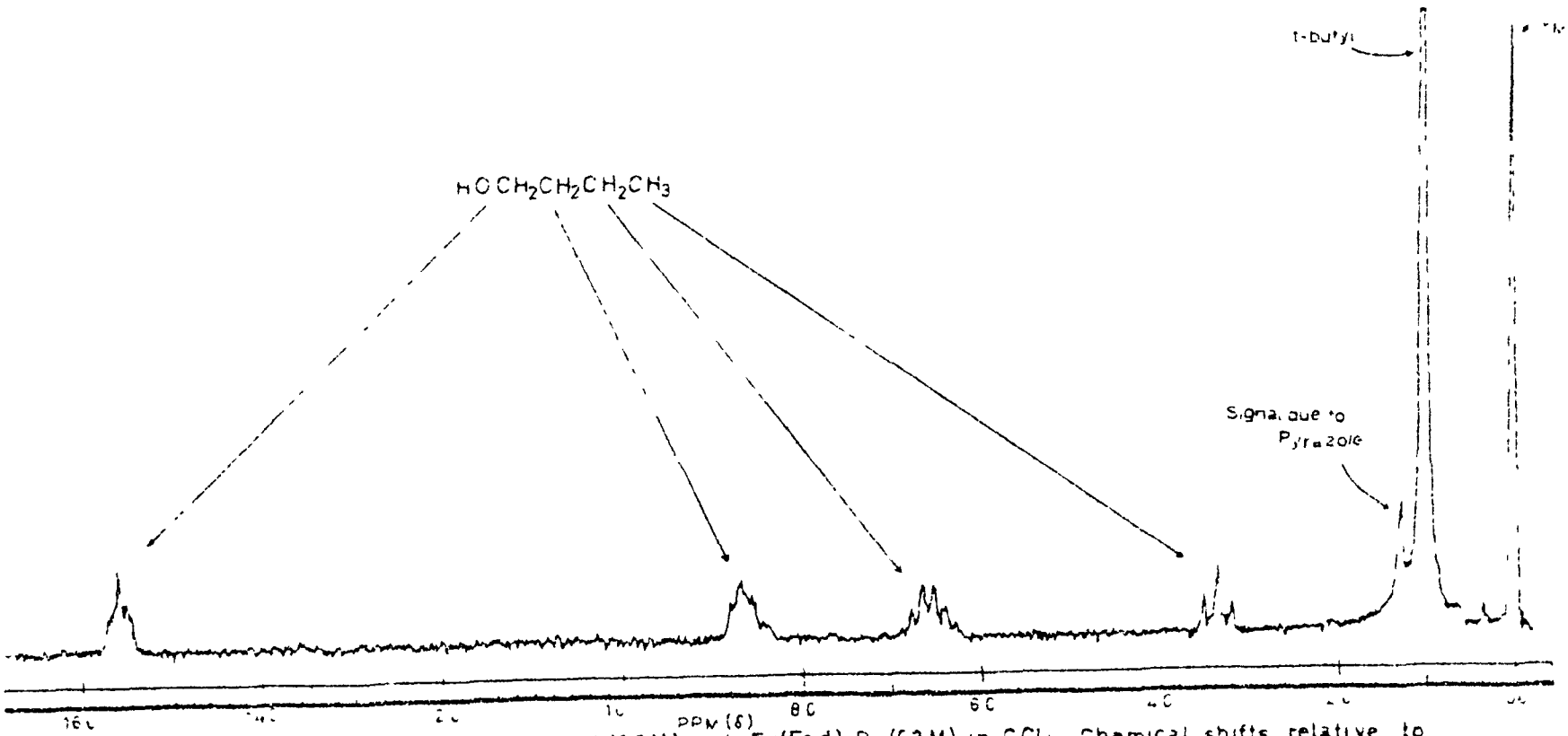

FIGURE 1 60 MHz ^{1}H nmr spectrum of n-butanol (0.2M) and $Eu(Fod)_3Pz$ (0.2M) in CCl_4. Chemical shifts relative to internal Me_4Si.

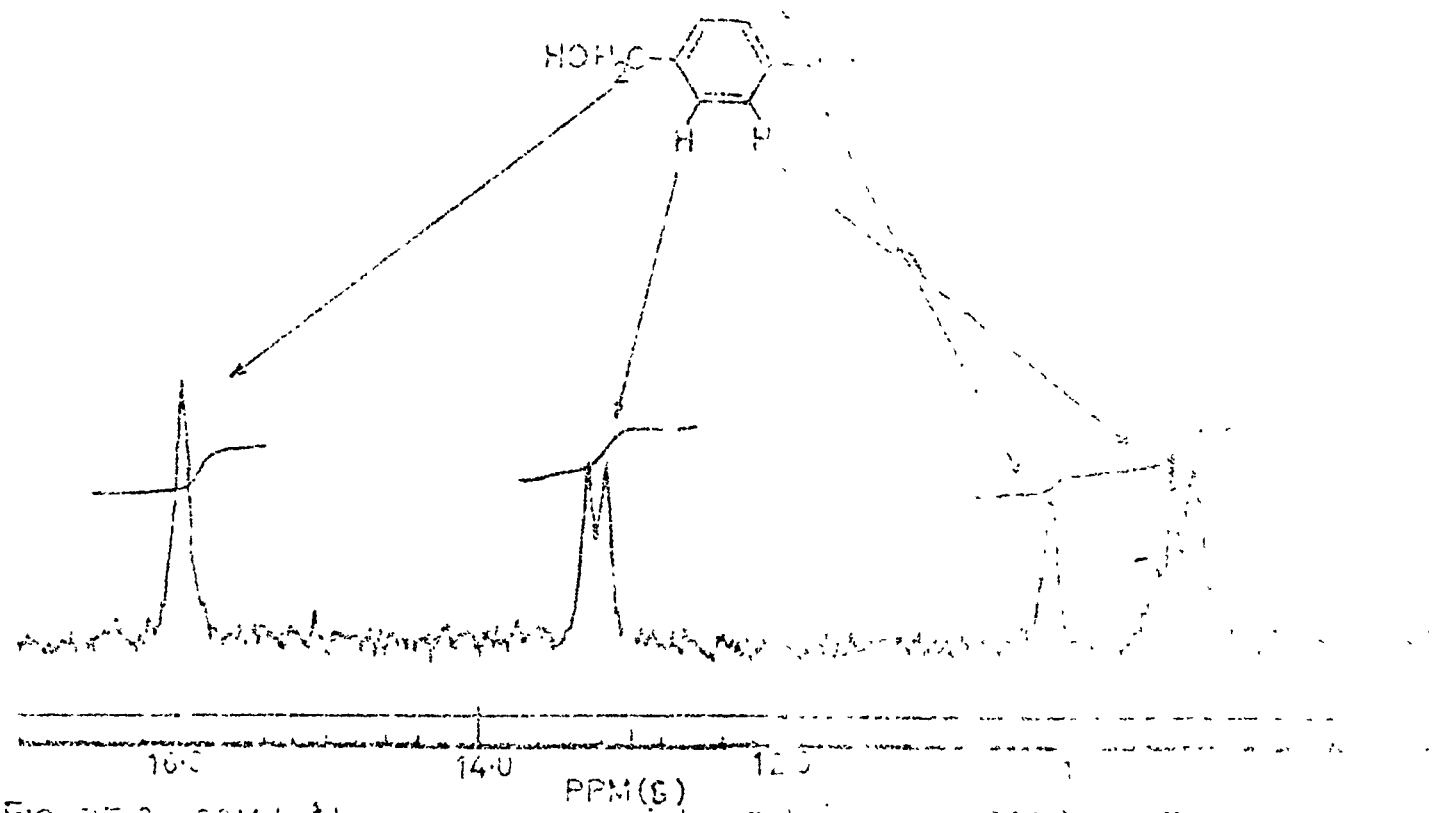

FIGURE 2. 60MHz ^{1}H nmr spectrum of benzyl [illegible] (CDCl$_3$) [illegible] Chemical shifts relative to internal Me$_4$Si

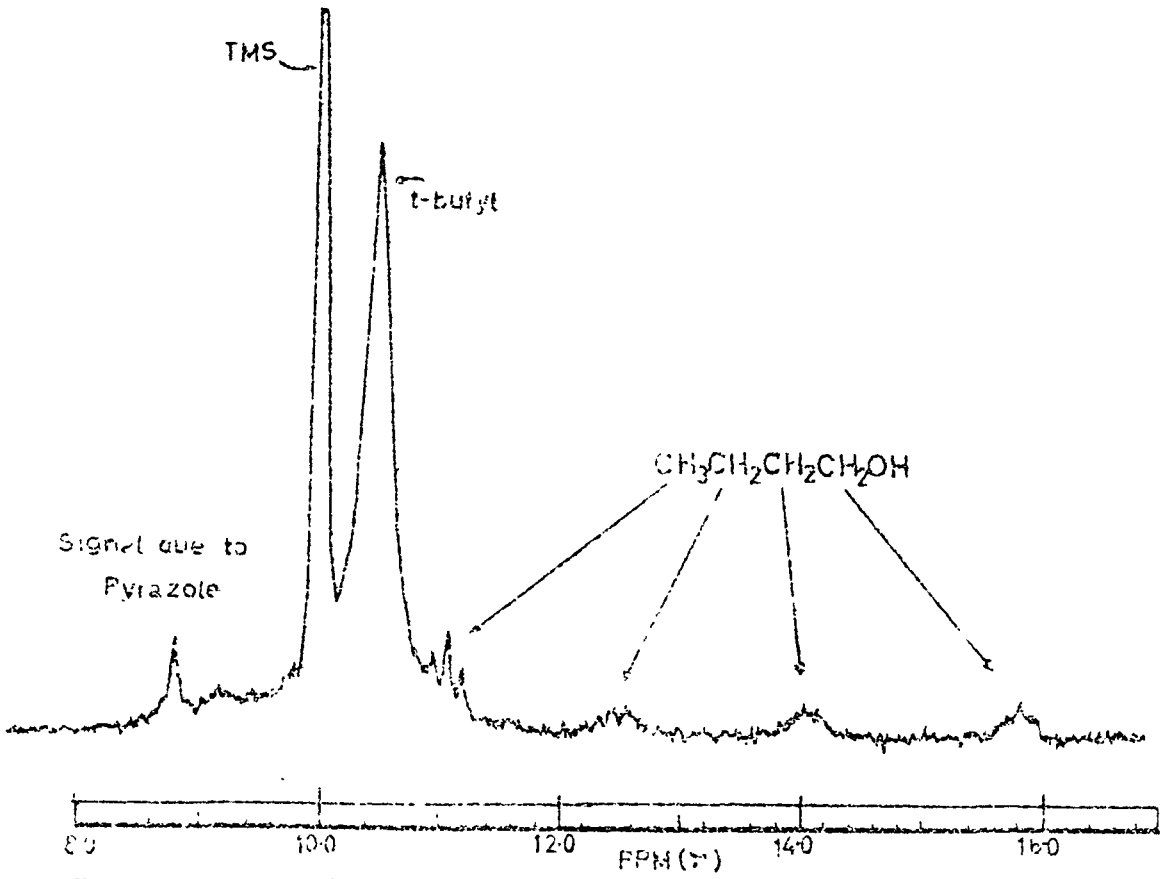

FIGURE 3. 60 MHz ^{1}H nmr spectrum of n-butanol (0·2M) and Pr(Fod)$_3$Pz(0·2M) in CCl_4. Chemical shifts relative to internal Me_4Si.

Table-1: Characterizing Data

Complexes	%Metal	%Carbon	%Hydrogen	%Nitrogen	ϕp_{Co}	Λ Ohm^{-1}cm^2 mole^{-1}	μ_{eff} (B.M)	Colour
Y(fod)$_3$Pz	8.52 (8.54)	38.20 (38.00)	3.18 (3.26)	2.70 (2.68)		-	Diamag.	White
La(Fod)$_3$Pz	13.33 (12.73)	35.87 (36.26)	3.33 (3.12)	2.58 (2.57)	209°	6.8	Diamag.	White
Pr(Fod)$_3$Pz	12.69 (12.89)	36.08 (36.20)	3.05 (3.11)	2.73 (2.56)	105°	16.3	3.67	Green
Nd(Fod)$_3$Pz	12.82 (13.13)	36.90 (36.10)	3.32 (3.10)	2.35 (2.55)	118°	9.9	3.81	Violet
Sm(Fod)$_3$Pz	13.60 (13.63)	35.83 (35.90)	3.10 (3.08)	2.58 (2.54)	112°	19.0	2.45	White
Eu(Fod)$_3$Pz	13.73 (13.76)	36.10 (35.84)	2.97 (3.08)	2.51 (2.53)	–	6.3	3.62	Light yellow
Gd(Fod)$_3$Pz	14.30 (14.16)	35.52 (36.68)	3.18 (3.06)	2.39 (2.52)	108°	6.8	7.96	Light yellow
Tb(Fod)$_3$Pz	14.33 (14.30)	35.83 (35.61)	3.26 (3.06)	2.51 (2.52)	-	-	9.87	Light yellow
Dy(Fod)$_3$Pz	15.18 (14.56)	34.98 (35.50)	3.18 (3.04)	2.47 (2.51)	139°	-	10.70	Light yellow
Ho(Fod)$_3$Pz	14.53 (14.76)	36.25 (35.42)	3.08 (3.04)	2.55 (2.50)	109°	10.0	10.55	Pink
Er(Fod)$_3$Pz	14.90 (14.92)	35.30 (35.36)	3.21 (3.03)	2.58 (2.50)	–	-	9.51	White
Tm(Fod)$_3$Pz	15.21 (15.06)	35.75 (35.30)	2.95 (3.03)	2.43 (2.50)	–	7.6	7.39	White
Yb(Fod)$_3$Pz	15.35 (15.36)	35.10 (35.10)	3.15 (3.02)	2.46 (2.49)	90°	-	4.50	White
Lu(Fod)$_3$Pz	15.30 (15.50)	35.29 (35.12)	2.98 (3.01)	2.50 (2.48)	–	-	Diamag.	White

Table -2: TGA Data for some of the complexes

Complexes	Temperature ^{o}C	% weight loss for Pyrazole
$La(Fod)_3Pz$	220^{o}	7.00 (6.22)
$Eu(Fod)_3Pz$	200^{o}	6.25 (6.15)
$Gd(Fod)_3Pz$	220^{o}	6.25 (6.12)
$Im(Fod)_3Pz$	200^{o}	6.00 (6.06)
$Yb(Fod)_3Pz$	200^{o}	5.75 (6.04)

Theoretical weight loss is in parenthesis.

Table -3: NMR Spectral Data[a]

Complexes	Signals due to Pyrazole			Signals due t ketoenolate	
	H-2	(H-3 & H-5)	H-4	CH	Bu^t
Pyrazole	13.73	7.57	6.26	-	-
$Y(Fod)_3Pz$	b	7.61	6.36	6.11	1.1
$La(Fod)_3Pz$	b	7.42	6.24	5.95	1.0
$Lu(Fod)_3Pz$	b	7.73	6.45	6.08	1.1
$Pr(Fod)_3Pz$	b	12.11	1.30	b	-0.4
$Yb(Fod)_3Pz$	b	34.92	3.18	b	3.7

[a] Obtained in Carbon tetrachloride at the probe temperature. Chemical shift in ppm down field from internal Me_4Si.

[b] Not observed

[c] in ppm up field w.r.t. Me_4Si

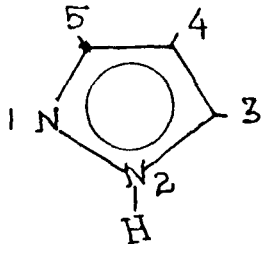

Table -4: $Eu(Fod)_3Pz$ Shifts in ppm downfield.

	H_α	H_β	H_γ	H_δ
n-Butanol	12.04	7.23	5.22	2.37
	CH_2	H_o	H_p	H_m
Benzyl Alcohol	11.33	5.89	2.89	2.04

Table -5: $Pr(Rod)_3Pz$ Shifts in ppm

	H_α	H_β	H_γ	H_δ
n-Butanol	-9.40	-5.90	-3.90	-2.06
	CH_2	H_o	H_p	H_m
Benzyl Alcohol	-6.77	3.14	1.09	0.78

negative sign indicate shifts up field w.r.t. Me_4Si and positive shifts are down field w.r.t. Me_4Si

Table -6: $Yb(Fod)_3P_z$ shifts in ppm down field.

	H_α	H_β	H_γ	H_δ
n-Butanol	28.67	27.82	17.82	8.92

Table -7 Covalency parameters

Complexes	$\bar{\beta}$	$b^{\frac{1}{2}}$	δ
$Pr(Fod)_3Pz$	0.98284	0.09262	1.74596
$Nd(Fod)_3Pz$	0.99598	0.04480	0.40322
$Er(Fod)_3Pz$	0.99225	0.06226	0.78139

Table -8 T_λ Parameters ($T_\lambda \times 10^8$)

Complexes	T_2	T_4	T_6
$Pr(Fod)_3Pz$	23.53370	0.11519	1.31464
$Nd(Fod)_3Pz$	75.40279	-195.39910	280.95548
$Er(Fod)_3Pz$	5.23880	0.80162	0.10367

Table -9: Oscillator strengths ($P \times 10^6$).

Complexes	S'L'J'	P_{Exp}	$P_{Calc.}$
$Pr(Fod)_3Pz$	$^1D_2$	4.57982	4.36339
	$^3P_0$	1.66622	3.90265
	$^3P_1$	2.20341	1.39446
	$^3P_2$	0.19348	0.19343
$Nd(Fod)_3Pz$	$^4F_{9/2}$	3.98525	16.10470
	$^2H_{11/2}$	32.38545	32.38533
	$[^4G_{5/2}, ^2G_{7/2}]$	54.78670	54.78660
	$^2K_{13/2}, ^4G_{7/2}, ^4G_{9/2}$	9.34646	9.34695
$Er(Fod)_3Pz$	$^4F_{9/2}$	7.22795	7.22794
	$[^2H_{11/2}]$	64.64725	64.64715
	$^4F_{7/2}$	4.70905	4.70905

Hypersensitive transitions are enclosed in parentheses.

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Bis-Acetylacetone Benzidine Complexes of Lanthanides: Synthesis and Spectral Studies.

Arvind, M. Sayeed, K. Iftikhar and N. Ahmad
Department of Chemistry, Aligarh Muslim University, Aligarh, (U.P.) India.

Abstract: Five coordinate bis-acetylacetone benzidine complexes of trivalent lanthanides are described. These complexes are characterized by their elemental analyses, molar conductances, i.r., electronic spectra, TGA and DTA. The magnetic moments are in solid state and in solution by n.m.r. method. Nephelauxetic parameter, $\bar{\beta}$ and Covalency parameter, δ, have been calculated and discussed.

Introduction: The Schiff base complexes of bisacetyl[illegible] and ethylenediamine with Cu, Ni, Pd and Ti are well kno[illegible][1-4]. Datt and Nag[5] have reported a new series of rare-earth metal chelates with salicylaldehyde and ethylenediamine and bis-acetylacetone and ethylenediamine. Mehta et al.[6] determined the stepwise formation constants of trivalent La, Ce, Pr and Nd complexes of acetylacetone-anthranilic acid and benzoyl aceto-nealanine. We studied the lanthanide complexes of bis-vanillin benzidine[7], bis-salicylidine O-dianisidine[8] and bis-vanilline-O-phenylenedimine[9]. We have also reported[4] complex of bis-

acetylacetone benzidine, ac_2bz, with Ti(III). The work on lanthanide metal complexes is still very scanty and needs to be done with variegated ligands. The present communication deals with the synthesis of the complexes of trivalent rare-earths with ac_2bz and their characterization by elemental analyses, molar conductances, TGA, DTA, magnetic moments, i.r. and electronic spectra. Some spectral parameters are also calculated for some of the complexes.

Experimental:

Rare-earth oxides (Leico chem. USA) converted to chlorides, benzidine (E. Merk), acetylacetone (E. Merk) and xylenol orang (B.D.H. England) were used in this study.

Synthesis: For the preparation of bis-acetyl acetone benzidine, to a well stirred solution of benzidine in ethanol was added acetyl acetone in the molar ratio of 1:2. The mixt was again heated and vigorously stirred on a hot plate for 4 hours when a curdy yellow precipitate separated. It was washed several times with ethanol. The crude product was crystallised in chloroform. Good crystalls were obtained by repeated crystallisation. The product was dried in vacuo over P_2O_5.

For the preparation of the complexes the ligand was refluxed in methanol for about 1/2 hr. and then the rare-ear

chloride solution in the same solvent was added. The ratio of the ligand and the metal salt was kept 1:1. The reaction mixture was refluxed for about three hours, and then kept for slow heating till a thick layer of the precipitate settled. The supernatant liquid was decanted off and the precipitate was washed with ethanol and chloroform in cold to remove any excess of ligand or metal chloride.

Methods: The complexes were subjected to elemental analyses for carbon hydrogen and nitrogen at this department and the metal was estimated with complexometric titration with EDTA using xylenol orange as the indicator. The melting points were measured by the usual method. The molar conductances of the complexes at 10^{-3}M dilution in dimethyl sulphoxide were measured using a Philips conductivity bridge model PR-9500. The magnetic susceptibility was determined with a Faraday balance at the Department of Chemistry, B.H.U. Varanasi and in few cases by Evans[10] n.m.r. method at varian A-60 n.m.r. machine at probe temperature in DMSO and diamagnetic correction was applied. The i.r. spectra of the ligand and the complexes were recorded in nujol mull with a Perkin Elmer i.r spectrometer in the range of 4000 cm^{-1} - 200 cm^{-1}. Electronic spectra were taken on Beckman DU-2 spectrophotometer. DTA and TGA were recorded at RRL Hyderabad.

Results and Discussion:

The analyses for the bis(acetylacetone) benzidine complexes of lanthanide (III) show a single chlorine per molecule of the complex. The molar conductances of the complexes are between 70.6—85.0 $ohm^{-1}cm^2$ $mole^{-1}$ in dimethyl sulphoxide at 10^{-3}M dilution. This is a range compatible with 1:1 electrolytes[11]. Hence the single chloride is outside the coordination sphere. The presence of a single chloride in the complexes of bis(acetylacetone) benzidine shows that the ligand interacts with the lanthanide ions in its enolic form and acts as a bifunctional tetradentate ligand. This seems to be quite plausible in view of the fact that complexation with enolic form leads to more extended π-bonding in comparison to the corresponding the keto form.

The magnetic moment of these complexes, when plotted against increasing atomic number, show the characteristic unusual double humped curve. Most of the values are from Faraday balance and in a few cases they are measured by n.m.r. technique. The two values in case of an element is quite close.

The bis-acetylacetone benzidine shows absorption at 1625, 1600 and 1550 cm^{-1} which are due to C=O, C=C and C=N stretchings respectively. The band at 1270 cm^{-1} may be due to the hydroxyl

group in hydrogen bonding in the enol form of the ligand. The two strong absorptions at 755 and 800 cm^{-1} are due to the CH deformation of the double bonded carbon in the hydrogen bonded ring. On complexation with trivalent lanthanide ions, the carbonyl absorption goes down in frequency by 20 to 30 cm^{-1} whereas the absorptions at 1600, 1550 and 1510 cm^{-1} generally do not appear but only a single weak and broad absorption is seen in this region. The band at 1270 cm^{-1} in the ligand also disappears in the complexes. The two bands at 755 and 800 cm^{-1} in the ligand are also present in the complexes with some shift in frequency since the complexes still have the CH at the double bonded carbon. The bands occurring at about 325 and 495 cm^{-1} are due to metal nitrogen and metal oxygen vibrations.

The lattice water absorbs at 3350-3200cm^{-1} (antisymmetric and symmetric stretching modes) and at 1630-1[illegible] cm^{-1} (H-O-H bending mode). Beside the fundamental mode of vibration coordinated water is expected to show other modes of vibration. The bands characteristic of coordinated water is seen near 1012 cm^{-1} and 965 cm^{-1} in K $[Cr(OX)_2(H_2O)_2]$. $3H_2O$[12]. We observed bands for coordinated water at 740-750cm^{-1} in $[Ln(TFAA)_3$ dipy $(H_2O)_2]$[13] and at 925-938cm^{-1} in $[Ln(Fod)_3$ dipy $(H_2O)_2]$[14] (TFAA = trifluoro acetylacetone, Fod = heptafluoro dimethyloctanedione and dipy = 2,2'-dipyridyl). The bands

occuring between 1025-1035cm^{-1}, mostly at 1030cm^{-1}, in these complexes does not have its equal in the ligand and are due to coordinated water. This is supported by TGA and DTA.

The thermograms of these complexes show a weight loss of about 3-4 % in the temperature range of 150-180°. The total weight loss is consistent with the loss of only one water molecule (theoretical weight loss for one water is 3.15-3.4). The one sharp DTA peak is identified in all cases in this temperature range. This and i.r. evidences show that only one water molecule is present in these complexes and which is inside the coordination sphere. All these evidences lead the formulation of the complexes as:

$$[Ln\ (C_{22}H_{22}N_2O_2.H_2O)]\ Cl$$

where Ln stands for trivalent lanthanide ions. The presence of one tetradentate $ac_2b\chi$ and one coordinated water in the molecules of these complexes makes the trivalent lanthanide ions five coordinate which is quite unfamiliar and uncommon. The complexes may have a tetragonal pyramidal structure with the ligand spanning the four basal and the water molecule occupying the apical position.

Electronic Spectra:

The electronic spectra of the complexes have been recorded in DMSO solutions as well as in the solid state. The intraligand bands occur in u.v. region and will not be discussed here.

The sharp line like internal $\underline{f} \rightarrow \underline{f}$ transitions originating with in the $4f^n$ configuration of the lanthanide (III) ions are affected by the influence of the ligands on complexation. A general feature in the spectra of lanthanide ions is enhancement of intensities of certain hypersensetive bands[15] and a shift of absorption bands towards lower wave number (nephelauxetic effect). It is usually assumed that the nephelauxetic ratio,

$$\left(\beta = \frac{1}{n}\sum_{n}^{n=1} \bar{\nu}^{i}_{comp} / \bar{\nu}^{c}_{aq.}\right)$$

is a measure of the metal ligand covalent binding[16] and is caused by a decrease in interelectronic repulsion parameter in the complexes[17]. The enhancement of intensity is ascribed by Jorgenson and Judd[15] as being due to pseudo quadrupolar effect originating in the inhomogenity of the dielectrics around the lanthanide ions.

It is expected that a general red shift of the $\underline{f}-\underline{f}$ transitions and an enhancement of the intensities of the certa

bands would be observed for the ac_2b_2 complexes. The spectra of Pr, Nd, HO and Er have been studied and a summary of the data ($\bar{\beta}$ and δ) is presented in table 2. The complexes do not show the usual red shift due to complexation and hence the values of $\bar{\beta}$ are greater than one indicating the ionic nature of these complexes. The Sinha's δ parameter[18] has negative values for these complexes indicating ionic nature of the complexes with respect to aquo ions.

Several bands of ac_2b_2 complexes, however, showed enhanced intensity. Such increase in intensity was also observed[19] for $^2G\,7/2$ and $^4G5/2$ bands of Nd(III) in [Nd (dpm)$_3$ Piperazine] (dpm = tetramethyl heptanedione). We found a four fold increase in the intensity of the same bands in [Nd (ac_2b_2) (H_2O)$_2$]Cl complex. The group of bands ($^2H11/2$, $^4G\,7/2$, $^4G\,9/2$) also showed an increase in the intensity.

The bands ($^1D_2$, $^3P_0$, $^3P_1$, $^3P_2$) of Pr (III) complex showed only slight increase in intensity compared to aquo ion. The intensity of $^5G6$ band of HO (III) complex is increased very much, the other bands seen in this complex are $^5F_2$, $^5S_2$, $^5F_3$, $^5G_5$ and $^3G_5$. The $^2H_{11/2}$ band, showed very much increase in intensity, in Er(III) complex, as compared to aquo ions. The other bands of Er(III) observed are $^4I\,9/2$, $^4F\,9/2$, $^4S\,3/2$, $^4F\,7/2$ and $^4F\,5/2$.

It seems that the $[Ln(ac_2bz)H_2O]Cl$ complexes represent a class of lanthanide complexes which shows pronounced enhancement of the f - f transition without causing any nephelauxetic shift. We also find that the shapes of the hypersensitive bands $^4G\,5/2$, $^2G\,7/2$ in Nd(III), the $^5G6$ band of HO(III) and the $^2H\,11/2$ band in Er(III) complexes are similar in the solid state and solution. This is evidence for the similarity in the environment around the metal ion in both states.

The results of i.r., TGA and electronic spectra have shown that our lanthanide complexes are five coordinate and have no possibility of hydrolysis as proposed by Nag[5] for the lanthanide (III) complexes of bis-acetylacetone ethylenediamine.

Acknowledgement: Arvind thanks the A.M.U. for providing financial assistance in the form of JRF and K.I. and M.I. thanks the CSIR, New Delhi, India for the award of research fellowships to them.

TABLE - 1 ELEMENTAL ANALYSES AND OTHER CHARACTERISING DATA

Name of Complexes	m.p. (°C)	M %	C %	H %	N %	Cl %	Molar Conductance in DMSO at 10^{-3} M
1. Ce (ac_2bz)H_2O Cl $C_{22}H_{24}CeClN_2O_3$	200	26.10 (25.95)	45.40 (48.95)	5.66 (5.44)	8.40 (5.18)	6.66 (6.56)	85.0
2. Pr (ac_2bz) H_2O Cl $C_{22}H_{24}ClN_2O_3Pr$	215	26.00 (26.09)	47.99 (48.83)	4.42 (4.44)	5.16 (5.18)	6.45 (6.51)	70.6
3. Nd (ac_2bz) H_2O Cl $C_{22}H_{24}ClN_2NdO_3$	210	26.60 (26.49)	48.52 (48.58)	4.38 (4.41)	5.13 (5.14)	6.42 (6.44)	76.6
4. Sm (ac_2bz) H_2O Cl $C_{22}H_{24}ClN_2O_3Sm$	206	27.28 (27.35)	47.35 (48.04)	4.32 (4.36)	5.06 (5.09)	6.32 (6.36)	85.0
5. Eu (ac_2bz)H_2O Cl $C_{22}H_{24}ClEuN_2O_3$	196	27.62 (27.56)	45.90 (47.90)	4.22 (4.35)	4.96 (5.07)		85.0
6. Gd (ac_2bz)H_2O Cl $C_{22}H_{24}ClGdN_2O_3$	192	28.20 (28.24)	46.55 (47.44)	4.23 (4.30)	5.01 (5.02)		[illegible]
7. Tb (ac_2bz)H_2O Cl $C_{22}H_{24}ClN_2O_3Tb$	211	28.50 (28.47)	45.78 (47.36)	4.27 (4.29)	4.93 (5.01)		[illegible]
8. Dy (ac_2bz)H_2O Cl $C_{22}H_{24}ClDyN_2O_3$	216	28.92 (28.91)	45.66 (46.99)	4.23 (4.26)	4.85 (4.93)	-	76.6
9. Ho (ac_2bz)H_2O Cl $C_{22}H_{24}ClHoN_2O_3$	218	29.31 (29.23)	45.76 (46.80)	4.24 (4.25)	4.88 (4.95)	-	76.6
10. Er (ac_2bz)H_2O Cl $C_{22}H_{24}ClErN_2O_3$	205	29.35 (29.48)	46.66 (46.60)	4.21 (4.23)	4.85 (4.93)	6.21 (6.25)	85.0
11. Tm (ac_2bz)H_2O Cl $C_{22}H_{24}ClN_2O_3Tm$	219	29.75 (29.78)	47.55 (46.47)	4.36 (4.22)	5.01 (4.92)	-	76.6
12. Yb (ac_2bz) H_2O Cl $C_{22}H_{24}ClN_2O_3Yb$	202	30.20 (30.23)	48.15 (46.13)	5.11 (4.19)	5.06 (4.88)	5.86 (6.19)	85.0

(ac_2bz) = bis-acetylacetone benzidine - H (enol form-H)

Results in parentheses are theoretical values.

TABLE 2. SPECTRAL PARAMETERS

	Pr (III)	Nd (III)	Ho (III)	Er (III)
$\bar{\beta}$	1.20	1.32	1.10	1.[illegible]0
δ	- 0.167	-0.24	-0.090	-0.236

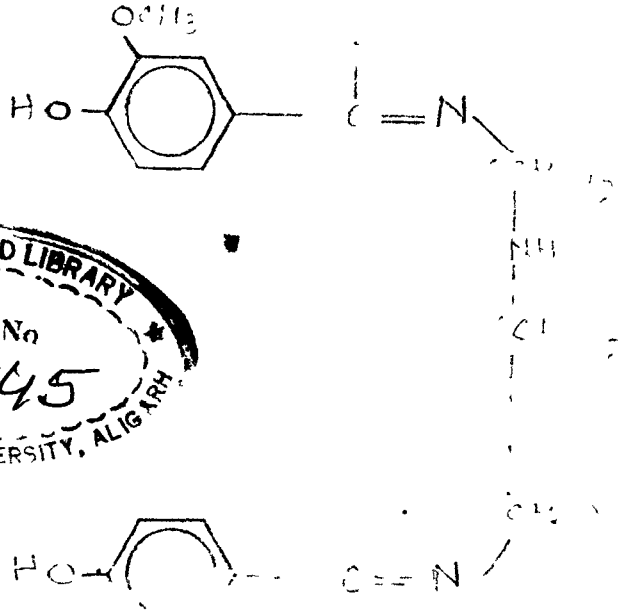
STUDIES ON COMPLEXES OF TRIVALENT LANTHANIDE IONS. IV. SCHIFF BASE DERIVED FROM VANILLIN AND TRIETHYLENETETRAMINE

ABU SHAIMA*, MOHAMMAD ATHAR & NASEER [illegible]

Department of Chemistry
Aligarh Muslim University, Aligarh.

A review of recent chemical literature [illegible] that comparatively less work has been reported on lanthanide(III) complexes of schiff bases[1-4]. Synthesis of lanthanide(III) [except Ce(III), Pm(III) & Lu(III)] complexes with the schiff base derived from vanillin and triethylenetetramine and their characterization are reported in this note.

The schiff base, (I) (van.trien) was prepared by the condensation of vanillin (Busch, Doake Allen, London) and triethylenetetramine (Riedel, Germany) in the molar ratio of 2:1 in ethanol and purified by recrystallization from the solvent by evaporation under reduced pressure.



The complexes were prepared by the reaction of the schiff base with rare earth chlorides ($LnCl_3$, from Leico Chemicals, U.S.A.) in ethanol in 1:1 mole ratio. The yellow precipitate obtained was washed several times with ethanol and dried *in vacuo* at room temperature. The complexes were analysed using standard methods. The analytical data are reported in Table 1.

The thermograms of the complexes were recorded (between ambient and 600°C) on a manual apparatus at R.R.L. Hyderabad. DTA were also carried out at R.R.L. Hyderabad using a Leeds and Northrup apparatus (between ambient and 600°C at a heating rate of 10°C/min.). Magnetic susceptibilities were determined at room temperature with a Faraday balance, at the Department of Chemistry, J.N.U. Varanasi. Molar conductance of 10^{-3}M solutions of the complexes in DMSO were determined with a Philips conductivity bridge, Model PR-9500, using a dip-type cell. Infrared spectra of the ligand and the complexes were recorded in nujol in the range 4000-200 cm^{-1} on a Perkin Elmer spectrometer, model 621. Reflectance spectra were recorded in the 200-900 nm at room temperature at G.N.D. University, Amritsar.

On the basis of analytical data and molar conductance (53-74 $ohm^{-1}cm^2mol^{-1}$) the complexes are represented as $[LnCl_2(van.trien)(H_2O)_2]Cl.H_2O$.

The ligand, van-trien shows bands at 1630 cm^{-1} (ν C=C & ν C=N), 1580 cm^{-1} (aromatic ring vibrations), 1505 cm^{-1} (N-H bending), 1270 cm^{-1} (in-plane bending of phenolic OH), 1155 cm^{-1} (C-aromatic-O-C-aliphatic), 1115 cm^{-1} (ν C-N) and 600 cm^{-1} (out of plane OH bending).

The 1630 cm^{-1} band shifts mostly to higher frequencies by about 10-70 cm^{-1} on complexation, whereas the 1580 cm^{-1} band remains almost unchanged and the band at 1505 cm^{-1} shows a positive shift of 10-15 cm^{-1} on complexation. The bands connected with the vibrations of hydroxyl groups remain almost unchanged on complexation. This shows that deprotonation of the hydroxyl groups does not occur and hence coordination of phenolic hydroxyl groups is unlikely. The shifts in C=N and N-H frequencies indicate the coordination through all the four nitrogens. In the IR spectra of the complexes, a band appears in the region of 950-820 cm^{-1} which may be due to coordinated water and a hump appears in the region of 3400-3300 cm^{-1} which may be due to non-coordinated water. Bands appear in the spectra of the complexes in the region of 320-300 cm^{-1} (metal-chlorine vibrations) and in the region of 410-375 cm^{-1} metal-nitrogen vibrations[10].

Thermograms of La(III), Pr(III), Nd(III), Sm(III) and Eu(III) complexes show peculiar features. In the lanthanum(III) complex, one water molecule is eliminated below 100°C, whereas the remaining two are eliminated at temperatures much above

100°C. Hence it is concluded that the two water molecules are coordinated, the third being just water of hydration. Thermograms of other complexes are similar. All the complexes, thus appear analogous and eight coordinated.

DTA curves show endothermic peaks at 280°, 300°, 315°, 280° and 315°C in the complexes of La(III), Pr(III), Nd(III) Sm(III) and Eu(III) respectively. These seem to denote elimination of the two $(OH)(OCH_3)C_6H_3$-CH-groups from the complex molecules.

Magnetic moments of the complexes when plotted against atomic numbers of the metal ions, give the usual unequal double humped curve.

Reflectance spectra of complexes of van-trien with Pr(III), Nd(III) and Sm(III) show charge-transfer bands[11] at 40815 and 29410 cm^{-1}, 40815 and 30770 cm^{-1}, and 40815 and 29850 cm^{-1} respectively. Other bands[11] are: (for Pr(III) complex) 25315 cm^{-1} ($4f \longrightarrow 5d$), 14495 cm^{-1} ($^3H_4 \longrightarrow {}^1D_2$); (for Nd(III) complex) 25000 cm^{-1} ($4f \longrightarrow 5d$), 17240 cm^{-1} ($^4I_{9/2} \longrightarrow {}^2G_{7/2}$); (for Sm(III) complex) 30315 cm^{-1} ($^6H_{5/2} \longrightarrow {}^4K_{11/2}$), 24690 cm^{-1} ($^6H_{5/2} \longrightarrow {}^6P_{3/2}$), 21740 cm^{-1} ($^6H_{5/2} \longrightarrow {}^4I_{13/2}$) respectively.

COMPOUNDS	De-comp. temp. (°C)	Found (Calc.),% C	H	N	Cl	$\mu_{eff.}$ in B.M.
$[LaCl_2(van.trien)(H_2O)_2]Cl.H_2O$	255	37.24 (37.00)	5.66 (5.05)	7.74 (7.85)	14.12 (14.93)	diamag.
$[PrCl_2(van.trien)(H_2O)_2]Cl.H_2O$	299	36.24 (36.90)	5.56 (5.03)	7.80 (7.83)	14.38 (14.89)	3.12
$[NdCl_2(van.trien)(H_2O)_2]Cl.H_2O$	225	36.00 (36.73)	5.45 (5.01)	7.68 (7.79)	-	3.81
$[SmCl_2(van.trien)(H_2O)_2]Cl.H_2O$	245	36.12 (36.42)	5.23 (4.97)	7.62 (7.72)	14.00 (14.69)	1.34
$[EuCl_2(van.trien)(H_2O)_2]Cl.H_2O$	260-62	35.24 (36.34)	5.12 (4.95)	7.66 (7.71)	-	3.77
$[GdCl_2(van.trien)(H_2O)_2]Cl.H_2O$	235	35.89 (36.08)	5.25 (4.92)	7.35 (7.65)	14.15 (14.55)	7.97
$[TbCl_2(van.trien)(H_2O)_2]Cl.H_2O$	215	35.28 (35.99)	5.11 (4.91)	7.23 (7.63)	-	10.17
$[DyCl_2(van.trien)(H_2O)_2]Cl.H_2O$	240	34.72 (35.82)	5.08 (4.88)	7.50 (7.59)	14.92 (14.45)	10.93
$[HoCl_2(van.trien)(H_2O)_2]Cl.H_2O$	240-42	35.00 (35.70)	4.96 (4.87)	7.47 (7.57)	-	10.69
$[ErCl_2(van.trien)(H_2O)_2]Cl.H_2O$	225	35.28 (35.59)	4.94 (4.85)	7.50 (7.55)	13.65 (14.36)	10.08
$[TmCl_2(van.trien)(H_2O)_2]Cl.H_2O$	229	34.21 (35.51)	4.99 (4.84)	7.42 (7.53)	-	7.90
$[YbCl_2(van.trien)(H_2O)_2]Cl.H_2O$	250	34.18 (35.31)	5.11 (4.81)	7.39 (7.49)	15.21 (14.25)	5.77

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Thorium (IV) and Dioxouranium (VI) Complexes with some Amines and Heterocyclic Bases

S.M.F. Rahman, Naseer Ahmad, Vijay Kumar* & M.M. Haq**
Department of Chemistry, Aligarh Muslim University,
Aligarh 202001
INDIA

SUMMARY

The complexes of thorium (IV) chloride and dioxouranium(VI) sulphate with a few bases — acridine, 2-aminopyridine, nicotinamide, piperazine, o-tolidine and o-dianisidine were synthesised, analysed and were found to have the composition $Th(Base)_2Cl_4$ and $UO_2(Base)SO_4.xH_2O$. The uranyl complexes with acridine and o-dianisidine were found to have one water molecule which was proved to be coordinated water on the evidence of thermogravimetric analysis. Molar conductances showed the thorium complexes to have two of the four chlorides outside the coordination sphere and the uranyl complex to have the sulphate outside it. I.R. spectra have been discussed to ascertain the coordination site.

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* Author to whom all correspondence should be addressed.
His present address : Chemistry Deptt.,S.V.College,Aligarh.

** Present address : Chemistry Deptt., Jamia Millia Islamia, New Delhi.

Standard 10^{-3}M solutions of the complexes were prepared in dimethyl formamide and their molar conductances were measured on a Philips PR 9500 conductivity bridge.

The thermograms of the complexes of dioxouranium(VI) with acridine, o-tolidine and o-dianisidine were taken between room temperature and 1000°C on a Dupont instrument 9500 at a heating rate of 15°C per minute.

The infra red spectra of the ligands and the complexes were recorded with Perkin-Elmer Infra Cord Model 137 B in the range of 4000 - 650 cm^{-1} using KBr pellets.

RESULTS AND DISCUSSION

The elemental analyses of the complexes of thorium(IV) chloride and dioxouranium(VI) sulphate with acridine, 2-aminopyridine, nicotinamide, piperazine, o-tolidine and o-dianisidine for carbon, hydrogen, nitrogen, metal (thorium or uranium) and the anion (chloride or sulphate), establish the compositions for the complexes as given in table No.1.

The molar conductance values of the complexes of thorium are in the range of 137.7 —157.2 and of dioxouranium in the range of 85.3—91.2. These values are compatible with 1 : 2 and 1 : 1 electrolytes as Geary[5] has reported molar conductances of 85 — 90 and 130 —170 ohm^{-1} cm^2 $mole^{-1}$ for 1 : 1 and 1 : 2 electrolytes in dimethyl formamide at 10^{-3} M dilution respectively.

Elemental analysis shows the presence of one water molecule in the complexes of uranium with acridine, o-tolidine and o-dianisidine. Thermogravimetric analysis shows weight losses of 3.18% (theoretical for one water molecule = 3.19%)

at 130°C in these complexes respectively. The water molecules in the cases of acridine and o-dianisidine are strongly bonded to uranium and hence must be coordinated.

In order to ascertain the bonding site in the complexes, the infra red spectra of the complexes were compared with those of the ligands. Acridine shows CC and CN at 1626, 1562 and 1515 which shift to 1634, 1618 and 1582 in thorium complex and to 1647 and 1592 cm^{-1} in uranyl complex. The ring vibrations and CH deformations also show shifts towards higher frequencies on coordination. The coordination of the metals with acridine through nitrogen is definite. The uranyl complex shows bands at 3413 and 3279 cm^{-1} which are absent in the ligand and must be due to water but the bands typical of coordinated water could not be located because of several other vibrations in this region. Thus thorium-acridine complex contains four coordinated thorium and dioxouranium complex contains four coordinated uranium.

The 2-aminopyridine absorbs at 3650, 3509, 3247, 3125 and 3077 (HNH and Ar(CH)), 1613, 1537 (NH deformations) and at 1111, 1093, 1081, 1036, 1010 and 1000 cm^{-1} (ring vibrations and CH deformations). The thorium complex shows bands at 3472, 1656, 1618, 1471 and 1370 cm^{-1} . The number of bands is very much reduced and there are considerable shifts in C = C, C = N, NH deformation and also in HNH stretchings. It is, therefore, concluded that coordination of thorium occurs at the heterocyclic nitrogen atom of the 2-aminopyridine and the other perturbations are due to the fact that the hydrogen bonding between pyridine nitrogen and the Hydrogen of NH_2 group breaks, thus making thorium tetra coordinate. Although the dioxouranium complex does not show such a decrease in the number

of bands, yet there are considerable shifts in the NH deformation and C = C and C = N stretchings in the complex. Hence it is presumed that coordination occurs at the heterocycli nitrogen atom making uranium tetracoordinate.

Nicotinamide contains three potential donor sites — the carbonyl oxygen of the amido part, the nitrogen of the NH_2 group, and the nitrogen atom of the pyridine part. The carbonyl oxygen may not be easily available because of some hydrogen bonding with the hydrogen atoms of the NH_2 group. Nicotinamide absorbs at 3472, 3247 (NH bands), 1667(CO stretchir 1608, 1587 (C = C and C = N stretchings), 1117 (CN) and at 1021, 699 cm^{-1} (Pyridine ring vibrations). In thorium complex the C = O absorption stays at the same position i.e., 1667 cm^{-1} showing thereby that the C = O does not play any part in coordination. The C = C and C = N vibrations are considerably perturbed. The C-N frequency goes down to 1111 cm^{-1} and asymmetric and symmetric NH stretchings appear at 3333 and 3175 cm^{-1} showing a lowering in the frequency on coordination. It may, therefore, be concluded that nicotinamide coordinates through the NH_2 and the pyridine nitrogen. The i.r. spectrum of dioxouranium(VI) complex shows similar features—3371, 3257-3155 (NH vibrations), 1681 (C = O stretching), 1623, 1605 & 1538 (C = C and C = N vibrations) and 1058 cm^{-1} (C-N vibration) and indicates coordination with both the nitrogen atoms of the nicotinamide, an observation in contrast to that of Konovalov et al[6]. The uranium is thus four coordinated.

The infra red spectra of thorium and dioxouranium complexes of piperazine present interesting features. Hendra and Powell[7] reported a chair form for piperazine for non-chelat

presence of a large number of bands in the complexes of piperazine by the formation of isomers of complexes involving axial and equatorial positions of the hydrogen atoms and metal ions about the nitrogen atom. Piperazine has also been reported to act as a bridging ligand[7,8] . The infra red spectra in the region of 4000-2800 contains three bands in piperazine, six in thorium and four in uranyl complex. Again in the region of 1700-1370 there are three bands in piperazine, six in thorium and four in uranyl complex and in the region below 1370 cm^{-1}, in NaCl region, there are five bands in the ligand, 18 in the thorium and 12 in the uranyl complex. This indicates that piperazine in thorium complex is monocoordinated so that the vibrations of one part of piperazine are effected and those of the other part containing N are not effected, raising the number of bands in the regions of -C-N and NH stretchings and NH deformations. The increase in the number of bands may also be due to the different arrangements of hydrogen atoms in axial and equatorial positions in various molecules of the same complex. Thorium is thus four coordinate. In the uranyl complex it may be assumed that the piperazine behaves as a bidentate ligand so that the vibrations due to both the nitrogen atoms are equally effected and the number of bands does not increase due to unequal shiftings of the bands of the two coordination sites of the piperazine. However, isomerism due to various equatorial and axial positions of hydrogen may be found in uranyl complex. Uranium is thus four coordinate in its complex.

The i.r. spectra of o-tolidine and o-dianisidine show a strong band at 1625 cm^{-1} which is assigned to NH_2 bending vibrations[9]. The band is shifted to lower frequency region on

Both o-tolidine and o-dianisidine act as bidentate ligands making uranium pentacoordinate and thorium hexacoordinate in these complexes.

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TABLE No. 1

Analytical Results and other Characteristic Data

Compound	Colour	Decompn. Temp. °C	Λ_M ohm^{-1} cm^2 mole^{-1}		% Metal	% Anion	% C	% H	% N
$Th(Acr)_2Cl_2]Cl_2$	Yellow	235-37	143.37	Calcd	31.69	19.37	42.65	2.48	3.85
				Found	31.65	19.37	42.95	2.42	3.80
$Th(Ampy)_2Cl_2]Cl_2$	White	167(m)	163.20	Calcd	41.28	25.25	21.37	2.15	9.96
				Found	41.21	25.23	21.31	2.11	9.97
$Th(Nic)_2Cl_2]Cl_2$	White	194-96	157.25	Calcd	37.54	22.94	23.31	1.95	9.06
				Found	37.59	22.99	23.33	1.97	8.71
$Th(Pip)_2Cl_2]Cl_2$	White	143(m)	146.20	Calcd	42.49	25.97	17.59	3.69	10.25
				Found	42.47	26.03	17.61	3.69	10.23
$Th(Tol)_2Cl_2]Cl_2$	White	250-52	156.88	Calcd	29.06	17.76	42.12	4.05	7.01
				Found	29.03	17.74	42.13	4.03	7.03
$Th(Dian)_2Cl_2]Cl_2$	Brown	234-36	141.18	Calcd	26.90	16.44	38.99	3.71	6.49
				Found	26.93	16.41	38.97	3.69	6.48
$UO_2.Acr.H_2O]SO_4$	Yellow	290-92	88.80	Calcd	42.25	17.05	27.71	1.96	2.48
				Found	42.25	17.03	27.67	1.96	2.49
$UO_2.Ampy]SO_4$	Yellow	265-67	85.31	Calcd	51.74	20.87	13.04	1.30	6.08
				Found	51.71	20.83	13.01	1.31	6.09
$UO_2.Nic]SO_4$	Brown	241-43	81.79	Calcd	48.75	19.66	14.76	1.24	5.74
				Found	48.75	19.61	14.71	1.27	5.75
$UO_2.Pip]SO_4$	Brown	285-87	79.51	Calcd	52.64	21.24	10.62	2.21	6.19
				Found	52.41	21.11	10.53	2.21	6.15
$UO_2.Tol.H_2O]SO_4$	Yellow	185-87	91.02	Calcd	39.91	16.10	28.19	3.04	4.69
				Found	39.91	16.08	28.16	3.05	4.71
$UO_2.Dian.H_2O]SO_4$	Grey	168-70	88.80	Calcd	37.87	15.28	26.75	2.88	4.45
				Found	37.88	15.26	26.76	2.89	4.42

m = melts